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**PHYSICAL SCIENCES**

Volume 6



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# PHYSICAL SCIENCES

Volume 6

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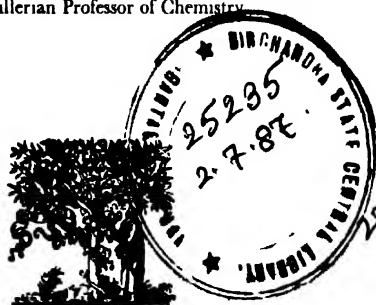
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# CONTENTS

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## 1903

Low Temperature Investigations—James Dewar . . . . .	1
Perfumes, Natural and Artificial—Adolf Liebmann . . . . .	10
Drops and Surface Tension—Lord Rayleigh . . . . .	15
Some Recent Investigations on Electrical Conduction — R. J. Strutt . . . . .	17
Recent Advances in Stereochemistry—William J. Pope . . . . .	24
Le Radium—Pierre Curie . . . . .	40

## 1904

Shadows—Lord Rayleigh . . . . .	54
Condensation Nuclei—C. T. R. Wilson . . . . .	62
The Motion of Viscous Substances—Frederick T. Trouton . . . . .	67
Liquid Hydrogen Calorimetry—James Dewar . . . . .	74
The Development of the Theory of Electrolytic Dis- sociation—Svante Arrhenius . . . . .	90

## 1905

New Low Temperature Phenomena—James Dewar . . . . .	104
High Power Microscopy—John W. Gordon . . . . .	120
The Structure of the Atom J. J. Thomson . . . . .	135
The Pressure due to Radiation—Ernest Fox Nichols . . . . .	150
The Development of Spectro-Chemistry—Julius Wilhelm Bruhl . . . . .	151

## 1906

Some Applications of the Theory of Electric Discharge to Spectroscopy—J. J. Thomson . . . . .	167
The Electric Production of Nitrates from the Atmos- phere—Silvanus P. Thompson . . . . .	181

The Passage of Electricity through Liquids—W. C. Dampier Whetham . . . . .	181
Recent Progress in Magneto-Optics—P. Zeeman . . . . .	190
Studies on Charcoal and Liquid Air—James Dewar . . . . .	210

## 1907

Rays of Positive Electricity—J. J. Thomson . . . . .	232
Studies in High Vacua and Helium at Low Temperatures—James Dewar . . . . .	248

## 1908

The Centenary of Davy's Discovery of the Metals of the Alkalis—T. E. Thorpe . . . . .	262
Recent Researches in Radio-activity—Ernest Rutherford . . . . .	273
The Ether of Space—Oliver Lodge . . . . .	287
Explosive Combustion, with Special Reference to that of Hydrocarbons—William Arthur Bone . . . . .	299
The Carriers of Positive Electricity—J. J. Thomson . . . . .	314
The Scientific work of William Thomson (Lord Kelvin)—Joseph Larmor . . . . .	345
The Nadir of Temperature and Allied Problems—James Dewar . . . . .	381
Low Temperature Research at the Royal Institution 1900–1907—Henry E. Armstrong . . . . .	391

Friday, January 16, 1903.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. F.R.S., Treasurer and Vice-President, in the Chair.

Professor SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*

*Low Temperature Investigations.*

IN the Friday Evening Discourse delivered in the year 1896, entitled "New Researches on Liquid Air" (*Proc. Roy. Inst.*), it was shown that seven substances, having very different coefficients of expansion, viz. cadmium, lead, copper, silver, calc spar, rock crystal, silver iodide, all gave the same density for liquid oxygen, when used to determine the weight displacement in the liquid, provided the correcting factor used in each case was the calculated mean coefficient of cubical expansion found by extending the values of Fizeau to low temperatures. The fact of the uniformity in the resulting oxygen density proved that the parabolic law of Fizeau may safely be used for extrapolation at low temperatures as far as the boiling point of air, especially in the case of the metals.

The determination of the densities of substances at the boiling point of oxygen—and hence of their mean coefficients of expansion between that temperature and ordinary temperatures—opens out a very large field of investigation, from which, if a sufficiently large number of observations were available, valuable deductions might be drawn. On account, however, of the expense and trouble of producing quantities of liquid oxygen, its use for this purpose is not likely to become general, although, when available, it is the easiest body to use in conducting such experiments, especially when the vacuum vessel containing it is immersed in a larger vessel containing the same fluid or well evaporated air. The ease with which liquid air can now be obtained in many laboratories suggests that its application to work of this kind would be a convenience. The use of a mixture of varying composition and density like liquid air necessitates a determination of its density with accuracy and rapidity before and during the course of the experiments. For this purpose, liquid air that had been allowed to evaporate for twenty-four hours in advance was used in large silver-coated vacuum vessels of some 3 litres capacity. In order to ascertain the density of the

liquid, a polished silver ball, which had been weighed once for all in liquid oxygen, was weighed in the sample of liquid air, and from the relative weights thus found the density of the liquid air could be approximately determined, that of liquid oxygen being 1.137. To prevent any disturbing ebullition in the liquid-air flask in which the weighings took place, and to reduce the rate of its evaporation to a minimum during the course of an experiment, the substance to be used was previously cooled in a supplementary vessel containing liquid air and then transferred to the large flask. Substances like solid carbonic acid and ice were weighed in the cool, gaseous air of the vacuum vessel, and their weights subsequently corrected for buoyancy. The temperatures of the densest and lightest samples of liquid air were ascertained by the hydrogen thermometer, and that of the others deduced by graphic interpolation. As the entire range of temperature through which the bodies were cooled amounted to about  $200^{\circ}$ , a degree or two up or down has no real influence on the results; the extreme range of temperature in the air samples was from  $83.8^{\circ}$  to  $86.1^{\circ}$  absolute.

Salts were employed in the form of compressed blocks. The salt, previously reduced to a fine powder, was moistened with water and compressed in a cylindrical steel mould under great hydraulic pressure. During compression the saturated salt solution drained away, and finally a cylindrical block of some 50 grammes of the salt was obtained free from porosity and hard enough to allow its surface to be polished. In this form salts and other materials similarly treated are especially adapted for accurate specific gravity determinations. After such treatment it was found that all the mechanically attached water was got rid of in the case of hydrated salts, and also in such as did not combine with water. In order to get cylindrical blocks of the salts showing no porosity, the presence of water, or rather the saturated salt solution, was found to be essential during the application of pressure. In the same way it was found to be an advantage in compressing such a substance as solid carbonic acid, to moisten it with a fluid like ether before applying the hydraulic pressure.

Recalling the work of Playfair and Joule,\* which originated in a suggestion of Dalton's that the volume of a hydrated salt in solution was simply the volume of the water of crystallisation as ice, some hydrated salts were selected, as well as some other bodies whose coefficients of expansion they had determined. Substances of special interest included in the list, were ice, mercury, sulphur, iodine, and solid carbonic acid, the latter being particularly important as an example of a solidified gas.

The specific gravity of the actual portion of the substance weighed in the liquid air was, with one or two exceptions, determined also at

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\* "Researches on Atomic Volume and Specific Gravity," Chem. Soc. Jour., vol. i., 121.



the temperature of the laboratory, about  $17^{\circ}\text{C}$ . From the two sets of observations the value of the mean coefficient of cubical expansion between  $17^{\circ}\text{C}$ . and the temperature of liquid air, was calculated, and whenever the expression coefficient of expansion is used, the volume coefficient is meant.

### ICE AT LOW TEMPERATURES.

The actual density at the temperature of liquid air of pieces of ice cut from large blocks, gave the value 0.92999. The density at  $0^{\circ}$  being 0.91599, this gives for the mean cubical coefficient 0.00008099.

We may take 0.0001551 as the mean coefficient of expansion of ice between  $0^{\circ}$  and  $-20^{\circ}\text{C}$ . Thus the mean coefficient of expansion between  $0^{\circ}$  and  $-188^{\circ}\text{C}$ . is about half of that between  $0^{\circ}$  and  $-20^{\circ}\text{C}$ . The mean coefficient of expansion of water in passing from  $4^{\circ}$  to  $-10^{\circ}\text{C}$ . is  $-0.000362$ , and from  $4^{\circ}$  to  $40^{\circ}\text{C}$ . it is 0.0002155. Hence the mean coefficient of expansion of ice between  $0^{\circ}$  and  $-188^{\circ}\text{C}$ ., is about one-fourth of that of water between  $0^{\circ}$  and  $10^{\circ}\text{C}$ ., and half of that between  $4^{\circ}$  and  $100^{\circ}\text{C}$ .

If the densities of ice at still lower temperatures could be determined, the values of the coefficient of expansion thence deduced would, we have every reason to believe, be less than the value given above. We shall therefore not be overstraining the case if we use the value just found to determine an upper limit to the density of ice at the absolute zero. The result is 0.9368, corresponding to a specific volume 1.0675. Now the density of water at the boiling-point, is 0.9586 (corresponding to the specific volume 1.0432), so that ice can never be cooled low enough to reduce its volume to that of the liquid taken at any temperature under one atmosphere pressure. In other words, ice molecules can never be so closely packed by thermal contraction as the water molecules are in the ordinary liquid condition, or the volume of ice at or near the absolute zero is not the minimum volume of the water molecules. It has been observed by Professor Poynting\* that if we suppose water could be cooled without freezing, then taking Brunner's coefficient for ice, and Hallstrom's formula for the volume of water at temperatures below  $4^{\circ}\text{C}$ ., it follows that ice and water would have the same specific volume at some temperature between  $-120^{\circ}$  and  $-130^{\circ}\text{C}$ . Applying then the ordinary thermodynamic relation, no change of state between ice and water could be brought about below this temperature. Clausius has shown that the latent heat of fusion of ice must be lowered with the temperature of fusion some 0.603 of a unit per degree. If such a decrement is assumed to be constant, then about  $-130^{\circ}\text{C}$ . the latent heat of fluidity would vanish. Thus under a pressure of about 16,000 atmospheres

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\* "Change of State, Solid, Liquid," Phil. Mag., 1881.

at this low temperature there ought theoretically, if the extrapolation pressure were legitimate, to be no distinction between the solid and liquid forms of water. At temperatures below this limit no amount of pressure would transform ice into water.

In inferring at what temperature this kind of critical point of the possible transition of ice into water takes place, no consideration of the change in the specific heats of ice and water under the greatly increased pressures have been included. If this is done, then it appears that ice under 50 tons and a corresponding temperature of about  $-50^{\circ}\text{C}$ ., would be all transformed into water, so that no lower temperature could be reached by any forced transition. All such speculations based on imperfect data are cleared away by the important experiment made by Tamman, who has shown that ice under a pressure of 20 to 30 tons on the square inch and a temperature of  $-22^{\circ}$  or  $-23^{\circ}$  becomes transformed into a new variety of ice, which under the specified conditions of temperature and pressure is denser than water. This new ice has a density greater than water, viz. 1.11, so that no amount of pressure on ice below the temperature of  $-23^{\circ}$ , can cause any transition. All the theoretical anticipations of the relations of ice and water at very low temperatures and high pressures have been entirely falsified by the results of Tamman.

Ice near its melting point can easily be squeezed into the form of wire when forced by hydraulic pressure from a steel cylinder having a small aperture in the bottom. If the temperature of the ice is lowered to  $-80^{\circ}\text{C}$ . by embedding the steel cylinder and plunger in solid carbonic acid under a pressure of 50 tons, the flow still takes place. The ice wire was now made up of what looked like a set of disc-like scales, which contrasted strongly in appearance with the transparent clear ice wire got when the experiment was made at  $0^{\circ}\text{C}$ . On cooling the ice and its accessories as above to a temperature approaching that of liquid air, no pressure the apparatus would stand caused any flow, but only intermittent explosive ejections.

Water was frozen in a steel cylinder in successive portions so as to include lead shot in the middle and upper portions of the ice, and the whole cooled to  $-80^{\circ}\text{C}$ . It was now subjected to 100 tons pressure in order to see if the lead spheres had fallen partly through the ice. After this great pressure the ice was clear, the lead spheres, however, had now very irregular shapes, but no motion of the kind anticipated had taken place. Thus ice under the pressure of 100 tons, or 15,000 atmospheres, which by theory ought to have lowered the melting point below  $-80^{\circ}$ , shows no such action. The transparent ice after the experiment showed no increase of density, but during the gradual heating up from  $-80^{\circ}$ , it became milk-white from some new crystalline arrangement. Such high pressure experiments are greatly favoured by the increased strength of the steel dies and pistons at the lowest temperatures.

Ice is a highly expansive substance, and as a result transparent blocks dropped into liquid air crack in all directions from the

sudden cooling. That the expansibility is being diminished at very low temperatures may be inferred from the fact that clear pieces of ice that have been slowly cooled to the temperature of liquid air when dropped into liquid hydrogen do not crack, although the relatively sudden drop in temperature is actually in this experiment greater than in the similar experiment with liquid air. The limiting density of ice at low temperatures may be determined from observing that it floats upon the surface of liquid oxygen, while it sinks in liquid nitrogen, the density of the former liquid being 1.13 and the latter 0.81.

#### SOLID CARBONIC ACID AT LOW TEMPERATURES.

The density of solid carbonic acid at its boiling-point was formerly given as 1.5,\* but the mean of my results came to 1.53. Recently the same value has been found by Behn. Taking this value and 1.6267, the density found at  $-188.8^{\circ}\text{C}$ ., the mean coefficient of expansion is found to be 0.0005704. This is a very large coefficient of expansion, being greater than that of any substance recorded in Table I. on page 423, and comparable with that of sulphur between  $80^{\circ}$  and  $100^{\circ}$ , which, according to Kopp, is 0.00062. The coefficient of expansion of liquid carbonic acid at its melting-point taken from the recent observations of Behn† is 0.002989, so that the rate of expansion of the liquid at its minimum value is very nearly five times that of the solid. When solid carbonic acid was subjected to pressure in the same steel cylinder as was used in the ice experiments, a wire of the solid, composed of a series of adhering disc-like plates, was easily formed.

#### COEFFICIENTS OF EXPANSION; HYDRATED SALTS; ORGANIC BODIES, ETC., AT LOW TEMPERATURES.

A general summary of the values found for the coefficients of expansion between  $17^{\circ}$  and  $-188^{\circ}$  of a number of substances is given in Table I. on page 423.

In the solid state mercury has a coefficient about half of that in the fluid state, while sodium has about the same value as that of mercury at the ordinary temperature. The coefficient for sulphur is about half of that between  $0^{\circ}$  and  $100^{\circ}\text{C}$ ., and that of iodine is not far removed from the value given for the solid at ordinary temperatures. The rate of expansion of liquid iodine is about three times this value. The value found for naphthalin is about half that of the liquid near its melting-point.

With the exception of carbonate of soda and chrome alum, hydrated salts have a coefficient of expansion not differing greatly from that of ice at low temperatures. It will be noted that iodoform is a highly expansive body like iodine, and that oxalate of methyl has

\* See Proc. Roy. Inst., 1878, "The Liquefaction of Gases."

† Chem. Jour., 1901.



### THE ACTION OF LOW TEMPERATURES ON METALS AND ALLOYS.

In a former discourse it was shown that all the chief metals and alloys acquired a greatly increased cohesive attraction at low temperatures as measured by the breaking stress. The increase in the breaking stress may reach from 30 to 50, or even 100 per cent. It was further shown that in some metals, before rupture took place at the temperature of liquid air, no diminution of the extension under stress had taken place as compared with similar tests made at the ordinary temperature. This led to testing the flow of a metal into wire about the temperature of liquid air. The only metal that could be examined in this way was lead. At the ordinary temperature in the apparatus used lead flowed into wire under a pressure of  $7\frac{1}{2}$  tons, but at  $-170^{\circ}$  C. it was necessary to apply the pressure of  $67\frac{1}{2}$  tons, or nine times the pressure, to cause any flow. In the same manner solder flowed into wire at the ordinary temperature when 35 tons was applied, but at the temperature of  $-170^{\circ}$  C. the application of 125 tons pressure caused no motion of the alloy through the aperture. This is the greatest pressure that any of the dies used in the experiments would stand without explosive rupture.

### COOLED RUBBER FILMS.

One of the most interesting illustrations of the increased strength and elasticity of a body at the lowest temperatures is to take the case of a very thin transparent film of indiarubber. The film is stretched over one end of a short glass tube about the diameter of a good wide test tube, the other end being contracted and sealed on to a long, narrow tube that after being bent twice at right angles, has still one limb more than 30 in. long. The film end of the test tube can now be immersed in liquid air, while the end of the long tube is placed in a vessel containing mercury, in order to observe the diminution of pressure in inches of mercury. When the whole test tube part covered by the film is cooled in liquid air, a diminution of from 9 to 10 in. of mercury may be observed. Under such conditions the film is perfectly tight, provided it has been tied on to the glass after a little coating of melted rubber has been applied to the surface. No liquid oxygen seems able to diffuse through the film, which is indeed remarkable considering the rapidity with which gaseous oxygen is known to pass. But the most remarkable fact of all is that the liquid air surrounding the film may be replaced by a vessel containing liquid hydrogen, which instantly solidifies all the air in the film-enclosed space, giving almost a perfect vacuum, as proved by the mercury column rising to the height of the barometer at the time, and yet the film stands the pressure when cooled to  $-252^{\circ}$  C., and further resists the passage of hydrogen by molecular diffusion. In the cooled

state such films, when struck with a cork hammer, give out a clear metallic ring, and if the striking is continued during the heating up of the film, a complete gamut of notes is produced from the varying elasticity. After returning to the ordinary temperature the film recovers all its ordinary properties.

### MOLECULAR VOLUMES AT THE ZERO OF TEMPERATURE.

Theoretical formulæ enable an estimate to be formed of the volume of the gram-molecule of many bodies at the zero of temperature. The direct experimental method is to ascertain the densities of bodies as near the zero of temperature as possible. By means of the use of liquid hydrogen as a cooling agent instead of liquid air densities might be determined within  $20^{\circ}$  of the zero. In the meantime the limiting densities of oxygen, nitrogen and hydrogen have been found, together with the coefficients of expansion about their boiling points. The approximate results are given in the following table:—

TABLE II.

	Density at Boiling Point	Density at $62\ 5^{\circ}$ Ab.	Density at $20^{\circ}$ Ab	Density at $15^{\circ}$ Ab.	Coefficient of Expansion.
Oxygen .. . . .	1.12	1.24	1.42	..	.004
Nitrogen .. . . .	0.80	0.88	1.03	..	.006
Hydrogen .. . . .	0.07	..	..	0.076	.013

Thus solid oxygen and nitrogen are respectively some 18 and 14 times denser than solid hydrogen, while the expansion coefficients of oxygen, nitrogen and hydrogen are roughly in the ratio of  $1, 1\frac{1}{2}$  and 3. With these values the molecular volumes at the absolute zero can be inferred, if we assume the general application of what is called the Matthias Law of the rectilinear semi-diameter. The values which result for oxygen, nitrogen and hydrogen are respectively 21.2, 25.5, 24.2. The volume in cubic centimetres of the gram-molecule of these three elements does not differ much from the mean value 23.6 c.c. The experiments already described on the density of ice and solid carbonic acid, about  $90^{\circ}$  absolute, enables an approximate estimate to be made of their zero volumes, which results in the values of 19.2 for the ice molecule and 25.7 for the carbonic acid one. From those values along with the molecular volumes given above, for solid hydrogen and oxygen, we can ascertain the volume change that would result in the formation of the compound molecules of ice and solid carbonic acid—provided they could be formed by an imaginary combination taking place, at the zero of the solid hydrogen and oxygen on the one hand, and the solid oxygen and carbon on the other. Thus

it appears that 100 volumes of mixed hydrogen and oxygen in the solid state would after combination produce 55.2 volumes of ice, or the contraction would amount to 45 per cent. of the initial volume of the mixture. This value is of the order of magnitude of the contraction which results from the combination of oxygen (solid) with metallic bodies like lithium and sodium, which is about 60 per cent. On the other hand, the production of solid carbonic acid from the diamond or graphite and solid oxygen, would in the former case involve an expansion of  $4\frac{1}{2}$  per cent., while in the latter the contraction would not exceed some 8 per cent. Such considerations confirm the view that what we call the molecular volume at zero is not the real volume of the molecules, but includes a considerable amount of unoccupied free space.

[J. D.]

Friday, February 27, 1903.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

ADOLF LIEBMANN, Esq., M.A. Ph.D. *M.R.I.*

*Perfumes, Natural and Artificial.*

HISTORY teaches that perfumes have been known and used ever since historical records have been kept. Even the Ayur Veda (the book of life), which contains the earliest traditions of the Sanskrit literature, mentions attar of roses, oil of antipogon and of calamus, and the way of producing them.

In the same way, the mythical documents of the ancient Persians prove that perfumes were known to them, but foremost among the ancient nations who were acquainted with perfumes, and their mode of production, were the Egyptians, who probably obtained them in a purified form.

The Egyptian culture spreading to Europe, imparted the knowledge of the East and the love for scents to their western neighbours, and Greece, as well as Rome, used, especially during the prosperous times, the extracts of flowers for perfumery as well as for medicinal purposes.

Later on, the Moors contributed largely to the evolution of knowledge on this subject, and Messne described in his book, 'Antidotarium,' in a special chapter 'De Oleis,' the preparation of essential oils.

In the middle ages, distillation, rediscovered in the fifteenth century, introduced the possibility of obtaining purer and more fragrant products, and as a consequence the production of perfumes proper was started as an industry in the south-west of France.

Scientific exploration of the chemistry of essential oils was, however, only possible after the great discoveries of Cavendish, Priestley and Lavoisier. From that time chemists began to devote their attention to perfumes, and their researches, although not explaining the structure and nature of these compounds, nevertheless contributed considerably to our knowledge of the subject. It was left to Wallach's and Bayer's classical researches to demonstrate the nature of terpenes, and their derivatives, which form part of nearly all essential oils.

Terpenes are cyclic compounds. Semler proved, on examining a number of alcohols and aldehydes, geraniol, linalool, citral and citronellal, frequently found in essential oils, that they belong to the



aliphatic series; and Thiemann, through his studies of vanilline, oil of iris and of irone, arrived at the synthesis of vanilline and ionone, or artificial violet. Many more might be mentioned as having contributed to our knowledge of this subject.

The chief sources of natural perfumes are the flowers, plants, aromatic roots, the sweet spices of the East, etc., from which the active principle, the essential oil, is extracted in different ways. The oldest method which is still in use for substances readily decomposable, and to which distillation with steam cannot be applied without destruction, is to treat the blossoms with vaseline or with molten fat, or press them between two sheets saturated with fat until the perfume has been completely dissolved in the fat (*enfleurage*).

The perfume can be separated from its fatty solvent by cold alcohol, in which the fats are insoluble. The essential oils of jasmine and tuberoses are, for instance, prepared in this manner. The mode is practically identical with the one described by Plinius in the second half of the first century.

The second mode of obtaining essential oils, and the one which is most generally used, is to distil the blossoms with steam. Attar of roses, oil of neroli, oil of lavender and many others are produced by this process. There are three distinct operations:

- (1) Preparation of the raw material.
- (2) Distillation.
- (3) Purification of the crude oil.

The distillation can be carried out

- (a) With high-pressure steam;
- (b) With superheated steam;
- (c) With water;

all of which may be used, but the selection must always depend on the properties of the oil.

The purification of the distillate is very important and must depend on the special impurities which may contaminate the oil.

A third mode of obtaining the perfume is to extract it from the raw material with low boiling liquids such as ether, petroleum ether or acetone, and to remove the solvent by evaporation, which is usually effected in *vacuo*.

An effort has been made to explain the fragrant properties of scents by the presence of aromatophoric groups in a similar way as the colour of substances is due to chromophoric groups, but not sufficient data have been collected to allow of any fixed conclusions.

A variety of classes of compounds have been isolated from essential oils such as hydrocarbons, alcohols, ethers, aldehydes, ketones, acids and their esters.

The most important hydrocarbons belong to the class of terpenes, and their complex structure has been explained by a series of clas-

sical researches by Wallach; they are cyclic compounds, and have the general formula  $C_{10}H_{18}$ .

Pinene, camphene, limonene, hipentene, phellandrene, sylvestrene, terpinene, are the terpenes more frequently occurring in essential oils.

Other hydrocarbons found in oils are sesquiterpenes,  $C_{15}H_{24}$ , and cadinene and caryophyllene are its chief members. Alcohols occur frequently either combined as acid esters, phenolic esters, or in the free state.

Of the greatest interest and importance are the diolefinic alcohols geraniol and linalool  $C_{20}H_{32}O$ , and the olefinic alcohol citronellol. Geraniol is the chief ingredient of attar of roses, and linalool is also present, but in smaller quantity.

Several modes of preparing these alcohols in pure state have been devised, and they can now be obtained in the market as chemical individuals.

Whilst these alcohols are open chain compounds, essential oils contain a number of cyclic alcohols which are true hydroxy derivatives of terpenes proper. Amongst the more important, terpineol, borneol and menthol may be mentioned.

Open chain aldehydes are substances of strong odour, not always very pleasant. Octyl and nonyl aldehydes are constituents of the German attar of roses and of oil of lemon. Citral, however, is more important, and occurs in nearly all essential oils, which are distinguished by the characteristic lemon odour of this substance.

It is contained, to the extent of from 70 to 80 per cent., in lemon grass oil, and its chief importance lies in the fact that it forms the raw material for the preparation of ionone or artificial violet.

Citronellal frequently occurs along with citral, and has similar properties.

A number of aromatic aldehydes, benzaldehyde, salicylic aldehyde, cumaric aldehyde, anis aldehyde, vanilline, heliotropin and cinnamic aldehyde belonging to the benzene series, occur in nature, but most of them are now prepared synthetically.

Of aliphatic ketones only methyl heptenone, distinguished by the fruity odour of amylacetate, and methyl nonyl ketone are of any importance. Cyclic ketones are, however, important constituents of some essential oils, for example, fenchone, tujone, pulegone, all distinguished by a characteristic smell. But the most valuable in the industry of perfumes is irone, the active principle obtained from the roots of violets, and ionone or artificial violet.

Acids as such do not assist the perfuming qualities of essential oils. They are either odourless or have an objectionable smell; but a number of esters have been found in natural perfumes and possess highly valuable properties; amongst them, methyl salicylate, methyl anthranilate, etc., and a number of esters of fatty acids.

Lactones are also represented amongst perfumes; sedanolide, with a strong odour of celery is present in this plant, and cumarine with

a refreshing odour of new hay, occurs in many plants, such as wood-ruff, tona beans, etc., and imparts to them their fragrance.

Phenols and phenolic ethers are very important members of the substances contributing to produce perfuming qualities.

Especially important are those which contain an olefinic side chain, such as anethol, eugenol, safrol, etc.

The examination of the natural perfumes was useful, not only as an extension of our knowledge of organic chemistry, but also for commercial reasons, that is, for the introduction of the synthetical essential oils into the market, reconstructed from the individuals found in the natural product. We are now able to buy a number of synthetical products, attar of roses, oil of jasmine, oil of neroli, etc.

But not only were the complex products of nature reconstructed synthetically, but the synthetical preparation of a number of chemical individuals was also successfully achieved, and vanilline was the pioneer in this direction.

Thiemann obtained it first by oxidation of coniferin or coniferil alcohol, and later on by the oxidation of acetisoeugenol. A number of other modes are now known, but Thiemann's latter process is technically still the most important one. The price of this aldehyde has fallen from 150*l.* in 1876 to 1*l.* 5*s.* to-day.

Heliotropin, protocatechu-aldehyde-methylene-ester, is likewise prepared synthetically by the oxidation of piperonic acid or by the oxidation of isosafrol; it forms, like vanilline, an example of the changes which are usually the result of competition, technical improvements and increasing consumption. Its price, which was once 75*l.*, has gone down to 15*s.* per pound.

Anisaldehyde and cinnamic aldehyde are now prepared in the laboratory. All these products, although artificial, are yet in another sense products of nature; that means, they are prepared synthetically, but they occur all of them in natural perfumes, and they have only been artificially produced for economic reasons.

But there are two scents of very great importance which are artificial in every meaning of the word: artificial musk and ionone, artificial violet.

Artificial musk, discovered by Baur, is trinitro-isobutyl-toluene or xylene, and is obtained by nitration of isobutyltoluene, isobutylxylene, and isobutylhydrindene.

There are a variety of these penetrating scents in which one of the nitro-groups is replaced by other groups, such as the cyanogen, halogen, ketonic and other groups, but the result from a perfuming point of view is identical.

Ionone, a ketone of the formula  $C_{13}H_{20}O$ , was discovered by Thiemann and forms the subject of a series of the most remarkable researches which this great scientist published.

It is obtained by condensation of citral with acetone, and by converting the new open chain ketone, which Thiemann calls pseudo-donone, into its isomeric ketone by treatment with acids.

Ionone is one of the finest perfumes in existence: it has the characteristic smell of violets and consists of two isomers, alpha and beta ionone, which in their perfuming qualities are practically identical.

There are some perfumes which are produced by animal life, such as musk, ambergris, but they have not yet been explored from a chemist's point of view.

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The Special Thanks of the Members were returned to The Worshipful Company of Clothworkers for their donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Friday, April 3, 1903.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. LL.D.  
F.R.S., President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, O.M.  
M.A. D.C.L. LL.D. Sc.D. F.R.S.  
PROFESSOR OF NATURAL PHILOSOPHY, R.I.

*Drops and Surface Tension.*

LORD RAYLEIGH introduced his subject by showing the well-known experiment of water rising inside a capillary tube to a higher level than that at which it stood outside, and explained the phenomenon as a compromise between the tendency of the water to come in contact with the glass, and thus creep upwards, and the tendency of gravity to pull it downwards. Water was a liquid which tended to wet glass, but if one, such as mercury, which did not have that tendency, were employed, the opposite effect was to be seen, and the liquid did not rise inside the tube so high as it did outside.

Lord Rayleigh then illustrated the effect of capillary attraction, or surface tension, in determining the formation of drops, and mentioned the part it played in soap-films. He next discussed some interesting phenomena depending on the contact of materials with water not perfectly pure. For example, fragments of camphor dropped on perfectly clean water immediately were set in rapid rotation. But if the surface were at all greasy, even to the extent that could be produced by dipping the finger in the water for a few seconds, the rotation stopped, to begin again if the greasiness were removed. He had calculated that a thickness of oil amounting to two-millionths of a millimetre was sufficient to stop the rotation from taking place.

Extremely small amounts of grease had no effect on the surface tension; the first degrees of contamination produced no alteration at all, and it was only after a certain quantity of grease had been added that the alteration was noticeable, though it then increased very rapidly. About half the amount of oil necessary to stop the camphor rotating was required to affect the surface tension. But one-millionth of a millimetre we might suppose to be about the diameter of an oil-molecule; hence, short of the point where the surface tension altered, there was only a single layer of oil-molecules on the water.

Why the surface tension was altered by a greater number might be indicated by an analogy. If a few marbles were floating sparsely on mercury, they did not offer any particular resistance if one pushed

them together to one side of the vessel ; but there was a resistance if they were so numerous as completely to cover the mercury surface, and if on being pushed together they had to mount one on top of the other.

Finally, Lord Rayleigh showed his audience the effect of dirt or grease in the liberation of gas from champagne or soda-water. The adherence of the bubbles, he was sorry to tell them, was a sign of the dirtiness of the glass, as he showed by putting in soda-water two iron rods, one treated so as to be free from grease and the other not, when the bubbles were seen adhering to the latter, but not to the former.

Friday, April 24, 1903.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

THE HON. R. J. STRUTT, M.A., Fellow of Trinity College,  
Cambridge.

*Some Recent Investigations on Electrical Conduction.*

WE have here a gold-leaf electroscope, which you can see projected on the screen. I charge it with electricity, and the leaves remain divergent. If, however, I touch the knob of the electroscope with my finger, or with any other conductor, the leaves at once collapse.

Now the knob is at all times in contact with the air of the room. We may infer therefore that if the air of the room conducts at all under the condition of this experiment, it can be only to a very slight extent.

If, however, air be submitted to very much greater electrical stress, quite a different state of things sets in. I have here a tube, containing rarefied air, which we will expose to a powerful electric stress, by connecting its terminals to those of an induction coil. You see at once that its insulation breaks down, and that it conveys the electric current, which produces brilliant and complex luminous effects in it.

These phenomena are of great interest and importance, and some light has been thrown on their cause and nature by recent investigations. But I do not propose to enter into such difficult questions to-night. We shall confine our attention to the behaviour of gases under small electromotive forces, such as are insufficient to produce luminous discharge.

I have explained that under these conditions the conductivity is very slight, or the leaves of the electroscope could not remain divergent. If, however, we expose the air to Röntgen rays, an immediate and most striking change in its electrical behaviour takes place.

You will see, in the gallery of the theatre, a bulb capable of emitting Röntgen rays. I charge the electroscope, and as soon as the bulb, many yards away, is set in action, the leaves collapse, showing that they have lost their charge. The air of the room, traversed by Röntgen rays, has lost its power of insulation, and the charge of the electroscope quickly leaks away through it. Almost immediately after the rays are turned off, the air recovers its insulating power, and as you see, the electroscope is again able to retain its

charge. Although the recovery of insulation is very rapid, it is not absolutely instantaneous. I have here an experiment bearing on this point. This metal box has a window of aluminium, through which the Röntgen rays can pass, so that the air in the box is exposed to them. This air is blown out through a considerable length of tubing on to the electroscope, and you see that it is able to discharge it. So that it is evident that some of the conducting power is retained during the time that the air takes to pass through about 2 feet of tubing, a considerable fraction of a second.

There is another way in which air can be made to lose its insulating power, and that is by exposing it to the action of the mysterious rays given out by radio-active bodies, notably by radium salts.

I charge the electroscope again, and you see that when I bring near it this sample of radium salt, the leaves fall together, as under the influence of Röntgen rays.

We may now consider more in detail the behaviour of gases made conducting by these methods.

When the electric current passes through a metal or an electrolyte, the relation between the current and the electromotive force applied is the simplest possible—the current is proportional to the electromotive force. The conductor is said to obey Ohm's law. But with a gas under the influence of Röntgen or Becquerel rays it is far otherwise. The current increases at first in proportion to the E.M.F., but when the E.M.F. is increased beyond a certain point, the current no longer increases correspondingly. Finally, when the E.M.F. is very large, a maximum value for the current is reached, and further increase in the E.M.F. is without influence upon it. The value of this limiting current, and the E.M.F. necessary to produce it, will of course depend on the strength of the rays. It is evidently of interest to compare the maximum or saturation current with different gases. Such comparisons have been carried out, and I will give you in a table some of the results.

Gas.	Relative Density.	Relative Saturation Current	
		Röntgen Rays.	Becquerel Rays.
Hydrogen . . . . .	·07	·10	·16
Air . . . . .	1·0	1·00	1·00
Sulphur dioxide . . . . .	2·19	8·73	2·32
Methyl iodide . . . . .	5·05	70·3	5·18

You will observe that, under the action of Becquerel rays, the saturation current is nearly proportional to the density, while, under



the action of Röntgen rays, a gas containing an element of high molecular weight, such as iodine, gives a current out of all proportion greater.

I wish now to return to a question which was too lightly passed over at the beginning of this lecture.

I said that the leakage of electricity through the air in its normal condition was very slight. But the existence of such a leakage has been incontestably proved.

The difficulty of establishing the conclusion is this. It is necessary to make use of some solid insulating support for the gold leaves of the electroscope. Now, if the leaves are observed to slowly collapse, it is difficult, with ordinary arrangements, to determine whether this leakage is really through the air or whether it takes place through the insulating support. This ambiguity of the experiment has been ingeniously overcome by Mr. C. T. R. Wilson, of Cambridge. His method was to carry the further end of the insulating support on a piece of metal which was at a higher potential than the gold leaves. Any failure in the insulation would then cause the leaves to diverge more than at first. It was found, however, that in fact the leaves collapsed in the course of a few hours. There could, therefore, be no doubt whatever that the charge was escaping through the air.

I have here an experiment which shows the same thing, though perhaps not quite so satisfactorily. There are two pairs of gold leaves, *a*, *b* (Fig. 1), in all respects similar. These are supported by clean ebonite insulators, *c*, *d*, exactly alike for each. The left-hand pair, however, hangs immediately from the ebonite support, while the right-hand one hangs from the support by a long wire *e*. The right-hand charged system, therefore, has much better access to the air than the left-hand one. And in the course of half-an-hour you will see that its leaves have collapsed much further, in spite of its greater electrical capacity.

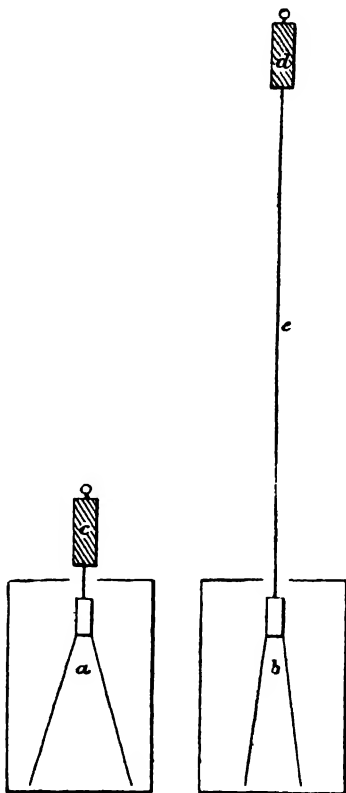


FIG. 1.

Mr. Wilson made a series of measurements of this electrical leakage through various gases, and he came to the interesting conclusion that the rates of leak were in the same ratio to one another as those which I had found for the same gases under the action of Becquerel rays. As a rule, the leakages were proportional to the densities of the gases, but as in the case of Becquerel rays, hydrogen was an exception, giving about twice as great a leakage as it ought to, if this law were exactly obeyed.

This curious agreement naturally suggested that the leakage ordinarily occurring was due to the same cause as the leakage under Becquerel rays. In other words, that the walls of the vessel containing the electroscope were giving off rays of this kind, although of course only to a very slight extent. In order to test whether this was really the case, I carried out a series of experiments on the rate of leak from a charged wire, when surrounded by cylinders of a uniform size, but of different materials. It soon became apparent that the rate of discharge depended on the nature of the surrounding wall.

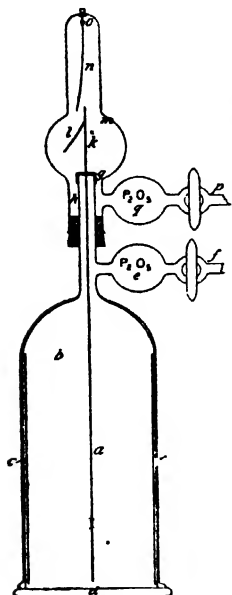


FIG. 2.

I will now show you a diagram of the apparatus used (Fig. 2). *a* is a charged wire in the axis of the cylindrical vessel *b*. The walls of *b* could be lined with any desired material by inserting a cylinder *c c* composed of it. This could be done by removing the glass plate *d* at the end, which was cemented on. The vessel could be exhausted through the stopcock *f* if desired. *e* was a drying bulb, containing phosphoric anhydride. The wire *a* passed air-tight through the brass cap *g*, cemented on to the neck *h* of *b*. *h* was made of lead glass, on account of the superior insulating qualities of this kind of glass. The cap *g* carried a brass strip *k*, to which the gold leaf *l* was attached. The whole was surrounded by a vessel *m*, as shown. *n* was an iron wire, attached to a platinum wire *o* sealed through the glass. The iron wire could be brought into contact with *k* by means of an external magnet, in order to charge the system. *m* could be exhausted through the stopcock *p*, and dried by means of the phosphoric anhydride contained in *q*. The position of the gold leaf was read by a microscope with micrometer eye-piece, focussed upon it.

Before making an experiment the insulation, which is all-important, was tested. *m* was permanently exhausted, and the stopcock *p* closed. *b* was also exhausted for the time, and a charge given to



the brass strip *k*, so that the leaf *l* diverged. It was found that the leaf moved over less than  $\frac{1}{8}$  of a scale division in the course of three hours.

As soon as any air was admitted into *b*, a leakage of electricity from the wire *a* was observed.

The following table gives the results, with various materials:—

Material of Cylinder.	Current, in scale divisions per hour.
Zinc . . . . .	1.2
Phosphoric acid on glass . . . . .	1.3
Aluminium . . . . .	1.4
Silver, chemically deposited . . . . .	1.6
Copper oxide . . . . .	1.7
Copper . . . . .	2.3
Tinfoil, 1st sample . . . . .	2.3
"    2nd sample . . . . .	3.3
Platinum, 1st sample . . . . .	2.0
"    2nd sample . . . . .	2.9
"    3rd sample . . . . .	3.9
Uranium nitrate . . . . .	12,000
Strongest radium preparations . . . . .	1,200,000,000

The number for uranium nitrate was obtained by cementing a small piece of the substance on to the inner wall of the cylinder, and determining the rate of leak. The number thus obtained was corrected to the value which would correspond to covering the whole cylinder with uranium nitrate. The value for radium is merely computed from the comparisons which have been made between radium and uranium.

We conclude, then, that the leakage always found in the air is not an essential property of the air itself, but is due to feeble radio-activity in the surrounding solid objects.

In the experiment I showed you, with the pair of gold leaves hung from a long electrified wire, the leakage was due to Becquerel rays emitted by the walls and floor of the room, and possibly even by the persons of the audience.

So far we have been speaking of gases of the ordinary kind, that is, the vapours of volatile inorganic substances.

There are, however, special reasons for thinking that a metallic vapour should behave differently in its electrical relations.

We will take mercury vapour as an example.

Let us suppose some mercury placed in a hermetically closed vessel, and let the vessel be heated. The mercury will partially evaporate, and, at any given temperature, there will be a definite density of vapour which is in equilibrium with the liquid, so that no further evaporation takes place. When the temperature is raised, the equilibrium vapour density increases, while the density of the liquid diminishes, so that, if the temperature be increased sufficiently, the liquid and vapour will have the same density, and will be indistinguishable from one another. The temperature at which this

happens is called the critical temperature. Now we know that the liquid mercury is an excellent conductor of electricity. Mercury vapour, however, as obtained by boiling mercury at the ordinary pressure of the air, does not conduct at all, or at least it only possesses the very feeble conducting power conferred on it by the Becquerel rays from the vessel walls, as I explained to you before. And yet, at the critical temperature, it must conduct as much as the liquid at that temperature, for indeed the two, liquid and vapour, are indistinguishable.

It is evident, therefore, that at these high temperatures and pressures, some very profound change must occur in the electrical properties of mercury. Either the liquid must be very much less conducting, or else the vapour immeasurably more so, than it would be under ordinary conditions. It might seem an easy matter to put this question to the test of experiment. But the practical difficulties are very great. It is necessary to confine the mercury in a closed vessel. This vessel must be capable of standing an enormous pressure; it must be able to stand a very high temperature without melting, and it must be made of electrically insulating material. These qualities cannot be found in sufficient degree in any known material. But they are most closely approached by vitreous silica, obtained by fusing rock-crystal in the oxy-hydrogen blow-pipe, and working it into tubes by the ingenious methods which were not long ago explained in this Institution by Mr. W. A. Shenstone.

I have here a tube of quartz, with thick walls. Some mercury has been hermetically sealed up in it. I place it over the flame of the blowpipe, and you see that the mercury, instead of boiling at a moderate temperature, as it would in an open vessel, is heated to full redness. In experimenting privately, I have been able to raise the temperature to a yellow heat. At that point the mercury vapour begins to show a steely blue absorption tint. Soon after this appears, the strongest tubes burst with the pressure of the vapour.

I will now show you a diagram of the tube used for measuring the electrical conductivity of mercury, and its vapour at a red heat (Fig. 3). The quartz tube took the form of an inverted Y, *a b b*. It was constricted to a very small diameter at the parts *d d* for a length of about 1 cm. on either side of the joint. The lower part of the limbs *b b* were of much larger diameter. The tube was filled with mercury up to the level *c*, the current being led in and out by iron wires *e e*, which projected some distance up, inside the arms *b b*.

The iron wires terminated in brass cups *f f*, carrying appropriate binding screws. These cups were filled with sealing-wax, which cemented them to the quartz tube. This sealing-wax had been sucked up the limbs while hot for a considerable distance, nearly up to the points *g g*, so as to fill the space between the iron wires *e e* and the lower parts of the quartz tube. The tops of the iron wires projected out through the sealing-wax, making contact with the mercury. The electrical resistance between the electrodes *f f* lay

mainly in the narrow portion  $dd$ , and this alone, with the branch  $a$ , was kept hot.

It was found that at a full red heat, the resistance of the liquid mercury was about doubled. The resistance of the saturated vapour was taken with the same apparatus, the narrow part  $dd$  being in this case filled with the vapour instead of the liquid; it was still ten

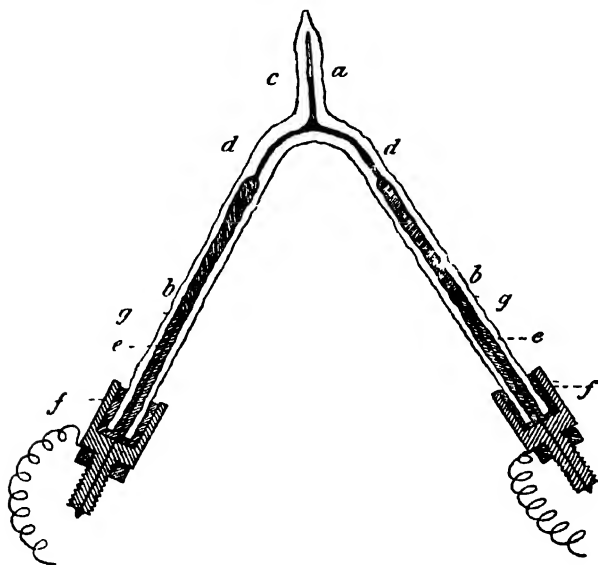


FIG. 3.

million times as great as that of the liquid. But the vapour did conduct very appreciably; and a current easily measurable with the galvanometer could be sent through it with a single battery cell. I think that in all probability, if we could trace the charge up to the critical temperature, we should find that the saturated vapour would approach in its electrical behaviour to the liquid metal.

Friday May 1, 1903.

SIR WILLIAM CROOKES, F.R.S., Honorary Secretary and  
Vice-President, in the Chair.

PROFESSOR WILLIAM J. POPE, F.R.S.

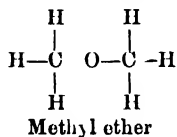
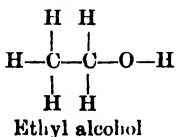
*Recent Advances in Stereochemistry.*

IN the year 1803, just a century ago, John Dalton delivered in the Royal Institution a series of scientific lectures during the course of which he doubtless laid before his audience a theory which he had just devised for the purpose of connecting together the vast number of isolated chemical facts known at the beginning of the nineteenth century. This theory, of which the centenary is being celebrated during the present month by the Manchester Literary and Philosophical Society, is known as the Atomic Theory, and was destined to form the foundation upon which the whole superstructure of modern chemistry has been built up. For our present purpose, Dalton's theory may be briefly stated in the form of the following two principles:—(1) Every element is made up of homogeneous atoms of which the mass is constant; (2) Chemical compounds are formed by the union of atoms of the various elements in simple numerical proportions. In accordance with Dalton's hypothesis, chemical substances may be mentally pictured by imagining the atoms as small spheres which have the power of aggregating themselves together under suitable conditions to form complexes or 'molecules'; thus, taking two similar spheres representing hydrogen atoms, in conjunction with a sphere of a different kind representative of an atom of oxygen, a chemical representation can be given of the compound water, the molecule of which is composed of two atoms of hydrogen and one of oxygen.

The original atomic theory offers no explanation of the observed fact that the atoms combine together in different proportions; this deficiency was remedied by the doctrine of 'Valency' enunciated by the late Sir Edward Frankland in 1852. Frankland supposed that the atoms of certain elements, such as hydrogen and chlorine, are unable to combine with more than one atom of any other element; these elements are termed monovalent. Other atoms, such as those of barium and zinc, can become directly attached to at most two other atoms; these are the divalent elements. Tri-, tetra-, penta-, hexa-, hepta-, and octa-valent elements can be similarly distinguished, the valency of hydrogen being taken as unity, in order to measure and

define the saturation-capacity or the atom-fixing power of the atoms of the other elements. It will be clear that for rough diagrammatic purposes we may provide the spheres representing the atoms with as many wooden pegs as the element itself exhibits units of valency; compound molecules can then be represented by fitting the atoms together by means of the pegs representing the number of valency units possessed by the various constituent atoms. By so doing a great advance is made upon the atomic theory of Dalton's time and a mental picture is obtained of the way in which the atoms are connected together within the molecule itself.

During the early part of the nineteenth century it became evident, principally from the work of Liebig and Wohler in Germany and of Faraday at the Royal Institution, that substances exist which possess totally different properties, but nevertheless have the same molecular composition; as this became slowly realised, the atomic theory was naturally called upon to furnish some adequate explanation. In view of the proven identity of molecular composition the required explanation could only be sought for in differences in the atomic arrangement within the molecules of the several substances. That such differences can be successfully illustrated by the aid of the atomic models will be seen on considering some specific case. Ordinary ethyl alcohol and methyl ether differ greatly from each other—the first is a liquid whilst the second is a gas at ordinary temperatures—but possess the same molecular composition, the molecule in each case consisting of two atoms of carbon, six of hydrogen and one of oxygen. These two substances have to be represented on the assumption that hydrogen is monovalent, carbon tetravalent and oxygen divalent. By joining wooden spheres together in the order shown in the figures—in which the valencies of the component atoms are carefully respected—diagrammatic representations are obtained which illustrate to the chemist the differences existing between ethyl alcohol and methyl ether. Substances related to each other in this

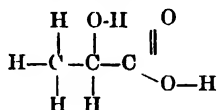


way are said to be isomeric; they have the same molecular composition but different molecular *constitutions*. The step in advance which is involved in thus writing molecular constitutions or in constructing molecular models was taken by Kekulé in 1858.

Two great stages in the development of chemical theory have now been indicated. First, that contributed by Dalton, who regarded constancy of molecular composition as characteristic of a chemical substance; secondly, that further stage, attained as a result of the labours of Liebig, Wöhler, Faraday, Frankland and Kekulé, which

involved the introduction of the idea that the chemical individuality of a substance is dependent upon its molecular constitution as well as upon its molecular composition. A third great development in the atomic theory had yet to take place.

Whilst the theoretical views which culminated in Kekulé's constitutional formulæ were at first found sufficient to explain numerous observed cases of isomerism, instances soon began to accumulate of substances which exist in so many isomeric forms that the Kekulé method of representation is incapable of accounting for them all. At an early date, Pasteur showed clearly that substances exist which have the same molecular composition and the same molecular constitution, but which nevertheless differ in important respects. A crisis was ultimately reached when, in 1870, Wislicenus demonstrated the existence of three isomeric lactic acids, all having the molecular composition,  $C_3H_5O_3$ , and the molecular constitution—



and contended that he had amply proved the insufficiency of Kekulé's method of writing constitutional formulæ.

The step needed to rid the atomic theory of these apparent anomalies was indicated by van't Hoff and Le Bel in 1874; they pointed out that the weakness of the Kekulé method lies in the tacit assumption that the molecule is spread out upon a plane surface: that by throwing this assumption aside and taking a rational view of the way in which the molecule is extended in space, all difficulties immediately vanish. The considerations put forward by van't Hoff and Le Bel form the basis of the subject now known as *Stereochemistry*, the branch of science which deals with the manner in which the atoms are distributed within the molecule in three-dimensional space; they deal, in the first place, with the arrangement of the constituent atoms in the simple organic compound, methane, the molecule of which has the composition,  $CH_4$ , or consists of one carbon atom and four hydrogen atoms. The Kekulé constitutional formula pictures the component atoms of the methane molecule as if joined together in one plane (Fig. 1), whilst according to the new view, the four hydrogen atoms are imagined situated at the four apices of a regular tetrahedron of which the carbon atom occupies the centre (Fig. 2). This is conveniently illustrated with the aid of a few cardboard models.

Consider now the result of replacing three of the four hydrogen atoms present in the methane molecule by three different groups of atoms—the three groups,  $CH_3$ ,  $OH$ , and  $CO_2H$ , for example. One of the most striking results which has accrued from the chemical investigation of the past century has been the demonstration of the



remarkable rigidity with which the atoms are held together in the molecule; it might therefore be anticipated that by actually making all the isomerides having the constitution indicated above, some means would be afforded of judging whether the van't Hoff-Le Bel

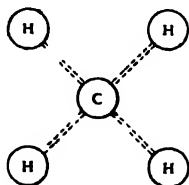


FIG. 1

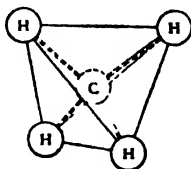
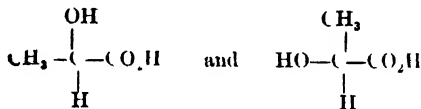


FIG. 2.

or the Kekulé view forms the closest approximation to the truth. Kekulé's constitutional formulæ indicate the existence of two isomeric compounds of the following types—



whilst, on the van't Hoff-Le Bel view, two isomerides should exist in which the four groups, H, CH<sub>3</sub>, OH, and CO<sub>2</sub>H, are arranged about the central carbon atom in the manner indicated in Figs. 3 and 4.

Although in each case two isomerides would be obtained, the examination of the two kinds of figure reveals very essential differences. The solid figure isomerides differ only in that the one is the image in a mirror of the other—they are related in the same kind of

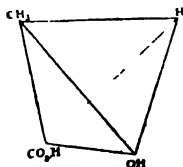


FIG. 3.

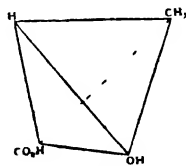
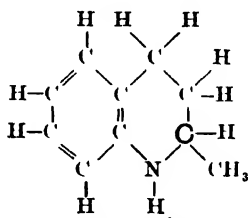


FIG. 4

way as a right- and a left-hand glove. The differences observable between two molecules thus related should consequently not be differences of an ordinary chemical nature, but differences involving merely a kind of chemical, physical and mechanical right- and left-handedness. The Kekulé constitutional formulæ, on the other hand, would indicate—if they indicate anything—that the substances to which they refer differ in the more gross way in which ordinary

chemical isomerides differ in chemical, physical and mechanical respects. That carbon atom which was present in the original methane molecule is, in these new compounds, now attached to four different atomic groups, and such a carbon atom is termed an asymmetric carbon atom. It is in the case of substances containing an asymmetric carbon atom that a lack of agreement is observed between the facts and the kind of isomerism indicated by the Kekulé formulæ, and in these cases also the species of isomerism indicated by the solid models exhibited is found to correspond closely with the facts.

To illustrate this, we may refer to a somewhat complicated substance termed tetrahydroquinaldine, which has the appended constitution and the molecule of which contains an asymmetric carbon



Tetrahydroquinaldine.

atom, that, namely, which is printed in heavy type. Three different isomeric forms of this substance exist and are quite indistinguishable by any of the ordinary methods of chemical or physical identification ;

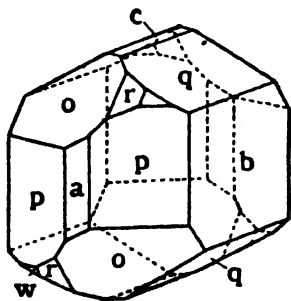


FIG. 5.

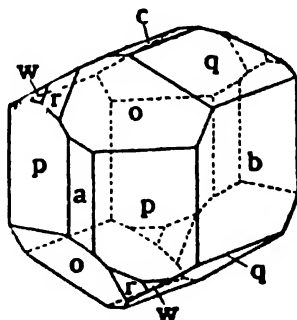


FIG. 6.

one of these is a loose kind of compound of the other two, and may therefore be disregarded for the moment. The remaining two have the same melting point, the same boiling point and correspond exactly in all ordinary properties ; they yield, however, series of derivatives

which differ in the same sort of way that a right-hand and a left-hand glove differ. Here, for instance, is a diagram showing the shapes of the crystals which these two substances form with hydrochloric acid (Figs. 5 and 6); the crystals obtained from the one base are the "mirror-images" of those prepared from the other. Any figure which possesses "handedness" of the kind exhibited by these two crystal figures is termed "enantiomorphous," and two figures which are related to each other as these figures are related are said to be enantiomorphously related.

A hand is thus enantiomorphous, and a right and a left hand are enantiomorphously related, the one being the mirror-image of the other. Here, for example, is a photograph showing a right and a left hand side by side (Fig. 7); the pair of hands is exactly reproduced in the next photograph (Fig. 8) which shows a right hand side by side with the photograph of its reflection in a mirror.

The conversion of a right- into a left-handed object and *vice versa* by reflection perhaps becomes more evident on considering the appended piece of ordinary print—right-handed print—(Fig. 9, B) and its mirror-image—left-handed print—(Fig. 9, A). On looking

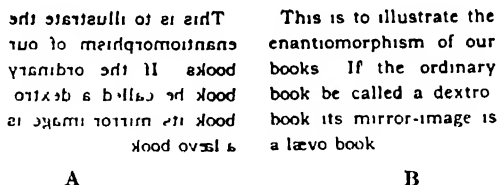


FIG. 9.

at the reflections of these in a mirror, A is seen reflected as right-handed print, whilst B becomes left-handed print, identical with the original A.

Just the same enantiomorphous relationship as that existing between the right and the left hand exists between the molecular pictures of the two lactic acids discovered by Wislicenus and shown in Figs. 3 and 4.

Reference may now be made to the existence of other differences of an enantiomorphous character between substances which possess enantiomorphously related structures. Early in the last century the French physicists Arago and Biot showed that a number of substances have the power of deflecting the plane of polarisation of a plane polarised light beam thrown through their solutions. Such substances are said to be optically active, and, since the deflection of the plane of polarisation may be either towards the right or towards the left, the exhibition of optical activity constitutes an enantiomorphous property; optically active substances are conveniently classified



FIG. 7.

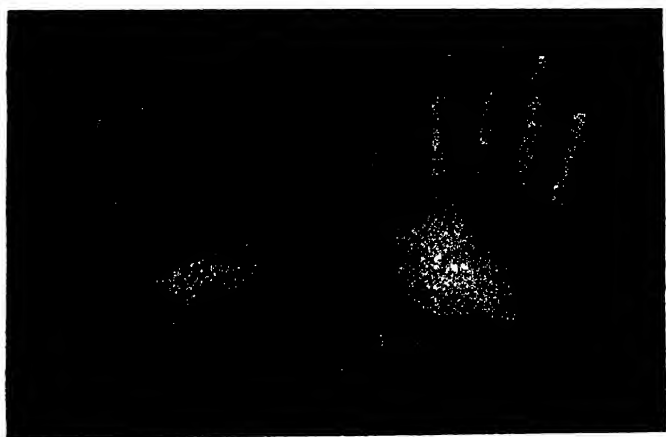


FIG. 8.

as dextro- and lævo-rotatory. Van't Hoff and Le Bel declared that the molecules of all naturally occurring substances which exhibit optical activity when in the fluid state contain asymmetric carbon atoms. All substances, the molecules of which contain an asymmetric carbon atom must possess enantiomorphous molecular configurations—similar to those assigned to the two lactic acids—because they exhibit properties of an enantiomorphous character.

A very beautiful experiment which the late Sir G. Gabriel Stokes devised and doubtless exhibited in this room may be so modified as to serve for the demonstration of optical activity. Stokes' experiment consists in passing a plane polarised beam of light through a tall cylinder containing water which has been rendered very slightly turbid by the addition of a little alcoholic solution of resin; a spectrum is then seen spread out in the column of liquid, and spread out in a way which is not enantiomorphous—the water possessing no optical activity. The modification of Stokes' experiment consists in replacing the non-enantiomorphous water by some enantiomorphous liquid—conveniently by a 70 per cent. aqueous solution of the dextro-rotatory cane-sugar or by a 50 per cent. solution of the lævo-rotatory fruit-sugar; on making this change, it is seen that instead of the spectrum lying in the cylinder\* vertically and therefore non-enantiomorphously, it winds spirally or corkscrew-wise round the column of the enantiomorphous liquid. These spirals or helices are clearly enantiomorphous and the two liquids of opposite optical activity give rise in this experiment to oppositely wound spirals—to spirals which are related to each other like the right- and left-handed corkscrews shown in the lantern slide. The opposite sign of the rotatory power exhibited by the cane-sugar and the fruit-sugar solutions is even more clearly shown by rotating the polarising prism in its mount, when the two spirals wind in opposite directions.

Although cases of optical activity are very frequently met with among chemical substances of animal or vegetable origin, it must be noted that no purely laboratory product or substance prepared without the use of enantiomorphous operations or materials is, in the ordinary way, optically active. The reason of this needs but little seeking if the solid models are once more consulted. Starting with a non-enantiomorphous substance is equivalent to starting with a methane derivative of the constitution—



and replacing one of the two X groups by the group Q, so as to obtain a compound containing an asymmetric carbon atom. Obviously,

\* In performing this experiment it is convenient to use a glass cylinder about 4 feet in length and 2½ inches in diameter, and to throw the polarised beam vertically through the column of liquid by means of a 45° prism.

unless some power of selection of an enantiomorphous nature is exercised in replacing X by Q, the doctrine of chance will ensure the one X group being replaced the same number of times as the other in an enormous number of tiny molecules. Thus there will result just the same amount of the right-handed optically active substance as of its left-handed isomeride. When an optically active substance is prepared in the laboratory it is therefore obtained as a mixture of two enantiomorphously related isomerides; such a mixture is said to be compensated, because the right-handedness of the one component is just counterbalanced by the left-handedness of the isomeric constituent. These compensated substances are represented by the third tetrahydroquinaldine previously referred to but not further discussed.

Since one of the great problems with which chemistry is grappling involves the synthetic preparation of naturally occurring optically active substances, it is of the utmost importance that the chemist should be in possession of working methods for resolving these compensated mixtures into their optically active components. All kinds of methods applicable to such resolutions necessarily involve the introduction of enantiomorphism—either of method or of material. Three types of method were introduced by Pasteur, namely, (1) spontaneous resolution by crystallisation, (2) resolution by combination with optically active substances, and (3) resolution by the action of living organisms.

The first kind of method depends upon the fact that on crystallising a compensated substance it sometimes deposits crystals of the dextro- and the lævo-isomeride side by side, and of such size that they can be mechanically sorted. The enantiomorphous factor determining the separation in this kind of method is obviously the enantiomorphous intelligence which has the power of discriminating between right and left-handedness. This sort of method is, unfortunately, but rarely applicable, owing to the fact that two enantiomorphously related substances usually crystallise together in the form of a loose chemical compound.

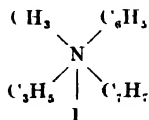
The second kind of Pasteur method is applicable to the resolution of compensated acids and bases, and depends upon the following considerations. On combining a compensated basic substance, viz. a mixture of d-B and l-B,\* with an optically active acid, say d-A, a mixture of two salts, namely, d-B, d-A and l-B, d-A, will be obtained. These salts, however, are not enantiomorphously related, as will be realised on substituting, for illustrative purposes, a hand for the base and a glove for the acid. The combination d-B, d-A will then be represented by a right hand in a right-handed glove, whilst the combination l-B, d-A will correspond to a left hand in a right-handed glove. The struggles of the left hand with the right-handed glove will not be a factor in determining the behaviour of the appropriately sorted right hand and right-handed glove. So also, the properties of the

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\* The prefixes dextro- and lævo- are conveniently abbreviated to the initials d- and l-.

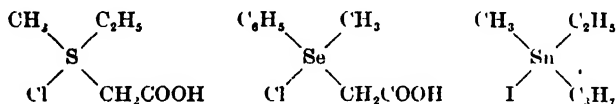
substance d-B, d-A—its solubility, melting point, etc.—will be conditioned by an enantiomorphous relationship of quite a different order from that determining the corresponding properties of the salt l-B, d-A; the solubilities, being determined by different factors, will naturally also differ, and the two salts will therefore be separable by crystallisation. The first resolution of a compensated base was effected by Ladenburg in 1885 and consisted in resolving the synthetic alkaloid coniine into its optically active components—one of which proved to be identical with the alkaloid contained in the juice of the hemlock—by crystallising it with d-tartaric acid. Since this date the methods of resolving compensated bases have been materially improved by the application of optically active acids derived from camphor for use in place of the dextro-tartaric acid, and an experiment in illustration can now be shown on the lecture table. On adding a solution of ammonium dextro-bromocamphorsulphonate to a solution of compensated tetrahydro- $\beta$ -naphthylamine hydrochloride, a white crystalline precipitate of d-tetrahydro- $\beta$ -naphthylamine d-bromocamphorsulphonate,—the salt d-B, d-A,—is thrown down, whilst the lævo-tetrahydronaphthylamine remains in the solution as its hydrochloride. The resolution in this, and in many other cases, can thus be very rapidly effected, and by still further applying the optically active camphorsulphonic acids a considerable extension of the original van't Hoff-Le Bel theory has become possible. These workers traced all cases of optical activity to the presence of an asymmetric carbon atom and deduced from their work the conclusion that the environment of the carbon atom in methane is a tetrahedral one. It is true that all the optically active substances which have yet been obtained from natural sources owe their optical activity to the presence of an asymmetric carbon atom, but it is important to note that by applying the second Pasteur method to the investigation of synthetic materials, compounds owing optical activity to the presence of asymmetric atoms other than those of carbon can be prepared.

Thus, ammonium iodide has the molecular composition  $\text{NH}_4\text{I}$  and, like methane, contains in its molecule four hydrogen atoms, which are replaceable by other atoms or groups of atoms; on replacing these hydrogen atoms by the four groups of atoms or radicles, methyl, allyl, phenyl, and benzyl, a substance is obtained which is conveniently named methylallylbenzylphenylammonium iodide and has the following constitution—



On replacing the iodine atom in this molecule by an optically active group of atoms, viz. by the dextrobromocamphorsulphonic

residue, two salts are obtained, each of which contains an optically active basic part and an optically active acidic part; these are salts of the kinds, d-B, d-A, and l-B, d-A, and can be separated by crystallisation from a convenient solvent, and after separation has been effected, each salt may be reconverted into the iodide. These regenerated iodides are found to be optically active in solution, and the conclusion is consequently drawn that optical activity is an attribute of the asymmetric pentavalent nitrogen atom as well as of the asymmetric tetravalent carbon atom. The optical activity of this substituted ammonium compound indicates that its molecule has an enantiomorphous configuration and is extended in three-dimensional space; the exact nature of this configuration is not yet known, inasmuch as a space arrangement of five groups is concerned, but the environment of the nitrogen atom in ammonium salts is clearly not a simple tetrahedral one. Just as enantiomorphism has been proved to be an attribute of the asymmetric nitrogen atom, we have also demonstrated that asymmetric tetravalent atoms of sulphur, selenium and tin give rise to optical activity; optically active substances having the constitutions shown below have been prepared, and we are thus well on the way towards obtaining a complete stereochemical scheme embracing all the elements.



It has been mentioned that optically active substances occur as such, rather than in the compensated form, in many animal and vegetable products, and also that when a substance containing an asymmetric carbon atom is prepared synthetically in the laboratory it is of necessity obtained in the compensated form or as a mixture in equal proportion of the dextro- and the lævo-isomerides. Taken together, these two facts have a very interesting bearing upon our speculations as to the origin of animal and vegetable life. Optically active substances have been isolated as products of the vital activity of all forms of animal or vegetable life which have been properly examined, but in spite of this, they are never obtained directly as laboratory products; some enantiomorphous influence has always to be exerted in their synthetic preparation, just as Pasteur applied enantiomorphism, either of method or of material, to the resolution of compensated substances. It was very strenuously argued by Professor Japp in his Presidential Address to the Chemical Section of the British Association in 1898, that no matter how successful we may be in reducing the problems relating to vital processes to mere questions of physics and chemistry, a residuum will always evade explanation by such means; this residuum will involve the discussion of the way in which the first enantiomorphous substance was resolved



into its optically active components. This question involves the introduction of an enantiomorphous agency at some period during the evolutionary development of living matter. In attributing difficulty to the solution of this residuary problem, Dr. Japp implies that the enantiomorphous agency, the co-operation of which is essential, must be an intelligent agency. Let us ask ourselves whether the enantiomorphous agency premised is necessarily other than one acting fortuitously. The assumption of a fortuitously enantiomorphous agency is certainly all that need be made to explain the building up of many enantiomorphous systems. The dead universe itself, as we know it, is enantiomorphous, but this fact has never been regarded as a valid argument against the current hypothesis as to the cosmic origin of our planet. Some degree of obscurity is, however, introduced into the discussion of the primitive origin of the optically active substances now produced by animals and plants by the probability that ages of evolution have transformed the primeval optically active substance into multitudes of other and more complex products, have, in fact, accentuated the enantiomorphism to such an extent that physiological chemistry is now almost entirely the chemistry of enantiomorphous substances. If in any particular case, however, we can show that an optically active substance can be locally accumulated, by the aid of some enantiomorphous agency acting purely fortuitously, it will be clear that the formation of the first optically active substance was not necessarily the work of an intelligent enantiomorphous agency. Such a species of separation of an optically active substance from a compensated one can be readily brought about in the laboratory. Pasteur showed that on crystallising the sodium ammonium salt of compensated tartaric acid (racemic acid) at ordinary temperature, large crystals separate; each of these consists of the salt of one or other of the d- and l-tartaric acids, the separation being brought about by the first of the Pasteur methods. If one of these crystals be selected casually, without the exercise of any selective intelligence, and used as a nucleus for inducing the crystallisation of further large quantities of the original solution, it will cause the separation of salt of its own kind; and ultimately a large quantity of salt of one of the optically active tartaric acids can be accumulated as the result of the introduction of an enantiomorphous agency such as might act fortuitously in a non-living universe. The probability of such a fortuitous agency arising would naturally be far greater in a living universe.

Again, suppose that, at its origin, life was carried on non-enantiomorphously, and that it involved the consumption and the production only of non-enantiomorphous substances and of compensated mixtures; it may well be foreseen that a stage in development might arise when each individual, in view of the increasing complexity of his vital processes, would have to decide to use only the one enantiomorphous component of his compensated food and so evade an otherwise necessary duplication of his digestive apparatus.

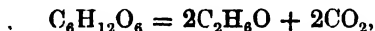
Acting unintelligently or fortuitously, one half of the individuals would become dextro-beings whilst the other half would become lævo-individuals; the succeeding generations would thus be of two enantiomorphously related configurations. It is, however, very difficult to believe that the natural selective operations which have been instrumental in conducting living organisms to their present stage of development, would allow the perpetuation of this state of affairs for any considerable period; some fortuitous enantiomorphous occurrence would temporarily give the one configuration the advantage over the other, an advantage which would be quickly accentuated and would involve the permanent disappearance of the weaker configuration.

The kind of difficulties involved in the existence, side by side, of individuals of dextro- and of lævo-tendencies, may be shown by a simple illustration. There is no reason connected with human enantiomorphism why vehicular traffic should be forced to keep to one side of the road rather than to the other; as, however, the conditions of civilised life have gradually become more complex, economic reasons have arisen forcing us to make an enantiomorphous selection and in this country we arbitrarily force the traffic to keep to the left; other countries also make an arbitrary, and sometimes a different, selection. Even if, when legislation on this matter first became necessary, the population had been equally and obstinately divided upon the question of the rule of the road, we cannot doubt that by this time the difficulty would have been satisfactorily and finally settled by the extermination of one or other of the enantiomorphously inclined parties without the co-operation of any intelligent enantiomorphous agency.

I mentioned that Pasteur gave a third method for the resolution of compensated substances, a method depending upon the selection exercised by living organisms upon the enantiomorphously related components of the mixture. He found, for instance, on allowing the mould *Penicillium glaucum* to grow in a solution containing compensated tartaric acid, that the mould used the d-tartaric acid as a food-stuff and rejected the lævo-isomeride, which latter could ultimately be separated from the solution. The kind of method thus indicated has been applied with success in a great number of cases, and is, in the end, merely a special application of Pasteur's second method. During recent years a considerable change has taken place in our views concerning the action of the lower organisms upon their food-stuffs. It was formerly supposed, for example, that the fermentation of sugar by an ordinary beer yeast is a part of the vital process of the organism itself, that the sugar taken in as food by the organism is finally thrown out in the form of carbon dioxide and alcohol; it is now clear, however, that the formation of these two products is in no way a vital process. On triturating yeast with powdered quartz so as to shatter the cell walls, and expressing the pulp thus produced, Buchner succeeded in obtaining a solution which, when mixed with sugar solution converts the sugar into carbon dioxide and alcohol. This fermentation is therefore not a vital phenomenon but is a

chemical action induced by some non-living substance contained in the expressed juice of the yeast cells. This substance—zymase—has been isolated in the solid state and belongs to the class of substances known as unorganised ferments or enzymes. Although many enzymes are known, each active in inducing the occurrence of some particular chemical change or changes, nothing is as yet known as to their molecular constitutions; ages of evolution have given such complexity to these substances that a century or less of chemical investigation has contributed practically nothing towards elucidating their nature.

During the investigation of great numbers of cases of animal and vegetable vital activity, instances of the action of enzymes have been found, the function of the enzyme being to bring about the molecular degradation and, in certain cases, the molecular complication, of more or less complex materials used or produced in the organism. As an example of molecular degradation due primarily to enzymic action, the action of zymase on grape sugar—d-glucose—may be quoted. In aqueous solution, one molecule of grape sugar becomes directly converted into two molecules of alcohol and two molecules of carbon dioxide, in accordance with the equation—



by the enzyme zymase. The enzyme itself suffers no permanent change as a result of exercising the power of causing this chemical reaction to take place, so that a comparatively minute quantity of the enzyme, acting for a more or less prolonged period, is able to convert an unlimited quantity of grape sugar into alcohol and carbon dioxide. The power which the enzyme possesses of inducing the occurrence of some chemical reaction which otherwise does not take place is not peculiar to enzymes; many substances, which are all classed together as the so-called catalytic agents, are known to exercise the same sort of influence in assisting a chemical reaction to occur. Thus the action of finely divided platinum in causing certain inflammable gases to ignite in air at the ordinary temperature is a catalytic action. The particular function exercised by enzymes in animal or vegetable life consists in bringing about chemical change quietly and continuously without necessitating the application of any violent chemical effects such as we are in the habit of using in the laboratory. Although they proceed so quietly, the chemical changes thus effected are, in many cases, changes which we have not yet succeeded in carrying out without the assistance of an enzyme; in the conversion of sugar into alcohol and carbon dioxide, zymase is performing a reaction which has never yet been brought about by the use of the ordinary laboratory methods.

Without quoting more specific instances, it may be generally stated that most of the cases of enzymic action hitherto investigated are cases in which a large molecular complex is degraded or broken down into substances of lower molecular weight. But it is important to note that the organism is also the seat of processes which result

in the building up of very complex molecules from simpler ones, such for instance, as the formation of starch from carbon dioxide and water. A specific case in which enzymic action leads to the production of a complex substance from simpler ones has been recently worked out by Fischer and Armstrong, who show that the enzyme, lactase, converts the sugar galactose,  $C_6H_{12}O_6$ , into a new sugar, isolactose,  $C_{12}H_{22}O_{11}$ , of nearly twice the molecular weight of the former.

All the enzymes with which we are acquainted appear to be enantiomorphous bodies; they are perhaps substances to which no definite molecular composition can ever be assigned, inasmuch as they may be systems consisting of a number of different true chemical compounds, the system being one which becomes endowed with extraordinary chemical activity when placed in a suitable environment. The enantiomorphism of the enzymes has been repeatedly demonstrated during the course of Emil Fischer's remarkable synthetic work on the sugars. Fischer succeeded in preparing fruit sugar by purely synthetical methods as a mixture of the dextro- and the lævo-isomerides; in order to isolate the previously unknown l-fructose he applied the third Pasteur method in that he cultivated a yeast in the solution of the compensated fructose. The yeast enzyme—presumably zymase—has arrived at its present stage of development by passing through countless generations, all of which have been fed upon sugars of the dextro-configuration, these being the only ones occurring in nature. In Fischer's experiment, the enzyme therefore readily devoured the d-fructose but refused to touch the l-fructose, which had never before been presented to it. The l-fructose was of course subsequently isolated from the solution. The need for compatibility between the enzyme and the material upon which it has to act is very elegantly illustrated by considering the effect of yeast upon a number of optically active and isomeric sugars. In the table are given the constitutions of a number of sugars of the composition  $C_6H_{12}O_6$ , the configurations of the three or four asymmetric carbon atoms present in the molecule being indicated by writing the hydrogen atoms on the right or the left of the figure, as the case may be.

COH	CH <sub>2</sub> OH	COH	COH	COH
H·C·OH	C:O	HO·C·H	H·C·OH	HO·C·H
HO·C·H	HO·C·H	HO·C·H	HO·C·H	HO·C·H
H·C·OH	H·C·OH	H·C·OH	HO·C·H	HO·C·H
H·C·OH	H·C·OH	H·C·OH	H·C·OH	H·C·OH
CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> OH
d-Glucose.	d-Fructose.	d-Mannose.	d-Galactose.	d-Triose.

The beer yeast ferments d-glucose, d-mannose and d-fructose, each of which contains a similar set of three asymmetric carbon atoms

in the molecule, with about equal facility; d-galactose is, however, only fermented with difficulty—of its four asymmetric carbon atoms, one differs in configuration from the corresponding one in the easily fermentable d-glucose; d-talose, in which two of the asymmetric carbon atoms differ in configuration from the corresponding atoms in d-glucose, is quite unaffected by the yeast. It is just as if the enzyme were provided with hands which enable it to grip the sugar molecule before tearing it to pieces; with these hands it grips the corresponding hands of, and so obtains a firm hold upon, the molecules of the first three sugars. The enzyme can only, however, grip the d-galactose molecule by two hands and so obtains a less firm hold. Owing to the greater incompatibility between the zymase and the d-talose the former obtains too feeble a hold on the latter to enable it to make a successful assault, and the sugar therefore remains unfermented.

The fact that the chemical reactions of animal and vegetable physiology consist in the main, of the production or destruction of optically active substances through the agency of enantiomorphous enzymes, is one of enormous importance. The complex substances concerned, such as starches, albumins and food-stuffs generally, occur in nature in but one of the enantiomorphously related configurations; all the albumins are lævo-rotatory, all the starches and sugars are derived from dextro-glucose. Since Fischer's work teaches us that none of the sugars derived from lævo-glucose are fermentable by yeast, it would seem to follow as a legitimate conclusion that, whilst d-glucose is a valuable food-stuff, we should be incapable of digesting its enantiomorphously related isomeride, l-glucose. Humanity is therefore composed of dextro-men and dextro-women. And just as we ourselves would probably starve if provided with nothing but food enantiomorphously related to that to which we are accustomed, so, if our enantiomorphously related isomerides, the lævo-men, were to come among us now, at a time when we have not yet succeeded in preparing synthetically the more important food-stuffs, we should be unable to provide them with the food necessary to keep them alive.

[W. J. P.]

Friday, June 19, 1903.

SIR WILLIAM CROOKES, F.R.S., Honorary Secretary and  
Vice-President, in the Chair.

Professor PIERRE CURIE, Faculté des Sciences à la Sorbonne, Paris.

### *Le Radium.*

#### I.

MR. BECQUEREL a découvert en 1896 que l'uranium et ses composés émettent spontanément des radiations qui présentent des analogies avec les rayons de Röntgen. Ces rayons nouveaux impressionnent la plaque photographique et rendent l'air qu'ils traversent conducteur de l'électricité. Ces rayons ne se réfléchissent pas, ne se réfractent pas, ils peuvent traverser le papier noir et les lames métalliques minces.\*

Les composés du thorium émettent des radiations analogues et d'une intensité comparable.† On a appelé *rayons de Becquerel* les rayons émis ainsi spontanément par certains corps, et nous avons appelé *substances radio-actives* les substances susceptibles de les émettre.

Nous avons découvert, Mme. Curie et moi, des substances radio-actives nouvelles qui ne sont qu'à l'état de traces dans certains minéraux, mais dont la radio-activité est très intense. Nous avons ainsi séparé le *polonium*, substance radio-active analogue au bismuth par ses propriétés chimiques, et le *radium* ‡ qui est un corps voisin du baryum. Mr. Debierne a depuis séparé l'*actinium*, substance radio-active que l'on peut rapprocher des terres rares. §

Le polonium, le radium, l'actinium émettent des radiations qui, comme ordre de grandeur, sont un million de fois plus intenses que celles émises par l'uranium et le thorium. Avec des substances aussi actives, les phénomènes de la radio-activité ont pu être étudiés en détail et un grand nombre de recherches ont été exécutées sur ce

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\* Becquerel, C.R. de l'ac. des sciences, plusieurs notes, 1896 et 1897. Rutherford, Phil. Mag., 1899.

† Schmidt, Wied. Ann., t. 65, p. 141. Mme. Curie, C.R. de l'ac. des sciences, avril 1898.

‡ Découvert dans un travail fait en commun avec Mr. Bémont.

§ P. Curie et Mme. Curie, C.R. de l'ac. des sciences, juillet 1898. P. Curie Mme. Curie et Mr. Bémont, C.R. de l'ac. des sciences, déc. 1898. Debierne, C.R. de l'ac. des sciences, oct. 1899 et avril 1900.

sujet par divers physiciens dans ces dernières années. Nous ne parlerons ici que du *radium*, parce que nous sommes parvenus à prouver que ce corps constitue un élément nouveau et que nous avons pu l'isoler à l'état de sel pur.\* Enfin, ce corps est celui qui a été le plus fréquemment utilisé dans les recherches de physique sur les propriétés des substances radio-actives.

## II.

Les rayons du radium impressionnent les plaques photographiques en un temps extrêmement court. L'action peut se produire à travers un écran quelconque. Les corps sont plus ou moins transparents, mais aucun écran n'est absolument opaque pour le rayonnement du radium.

Les rayons du radium provoquent la phosphorescence d'un très grand nombre de corps : sels alcalins, alcalino-terreux, matières organiques, peau, verre, papier, sels d'urane, etc. ; le diamant, le platinocyanure de baryum et le sulfure de zinc phosphorescent de Sidot sont particulièrement sensibles. Avec le sulfure de zinc phosphorescent la luminosité persiste assez longtemps quand on supprime l'action des rayons du radium.

Le rayonnement du radium est aussi intense quand le radium est placé dans l'air liquide (à  $-180$ ) que quand il est à la température ambiante. Voici une expérience qui montre les effets du rayonnement aux basses températures : on place au fond d'une éprouvette en verre une ampoule contenant un sel de radium et un petit écran au platinocyanure de baryum que le voisinage du radium rend lumineux. On plonge ensuite l'éprouvette dans l'air liquide et l'on constate que l'écran au platinocyanure de baryum est au moins aussi lumineux qu'avant l'immersion (expérience). Quand on répète cette expérience avec un écran au sulfure de zinc de Sidot, la luminosité de l'écran diminue fortement à la température de l'air liquide, mais cette diminution est due à la baisse du pouvoir phosphorescent du sulfure de zinc aux basses températures.

Les substances phosphorescentes sont, peu à peu, altérées par une action prolongée des rayons du radium, elles deviennent alors moins excitables et sont moins lumineuses sous l'action de ces rayons.

Les sels de radium sont spontanément lumineux ; on peut admettre qu'ils se rendent eux-mêmes phosphorescents par l'action des rayons de Becquerel qu'ils émettent. Le chlorure et le bromure de radium anhydres sont les sels qui donnent la luminosité la plus intense. On peut en obtenir d'assez lumineux pour que la lumière puisse se voir en plein jour. La lumière émise par les sels de radium rappelle alors comme teinte celle émise par le ver luisant (lanipyre). La luminosité des sels de radium diminue avec le temps sans jamais disparaître complètement, et en même temps les sels d'abord incolores se colorent en gris, en jaune ou en violet.

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\* *Mme. Curie*, Thèse à la Faculté des sciences de Paris, 1903.

## III.

Les rayons du radium rendent l'air qu'ils traversent conducteur de l'électricité. Quand on approche quelques décigrammes d'un sel de radium d'un électroscope chargé, celui-ci se décharge immédiatement. La décharge se produit encore, bien que plus lentement, lorsque l'on protège l'électroscope par une paroi solide épaisse. Le plomb, le platine absorbent fortement les radiations; l'aluminium est le métal le plus transparent, les corps organiques absorbent relativement peu les rayons de Becquerel (expériences).

Les rayons du radium rendent également légèrement conducteurs les liquides diélectriques tels que l'éther de pétrole, le sulfure de carbone, la benzine, l'air liquide.\*

Les rayons du radium dans certaines conditions facilitent le passage de l'étincelle entre deux conducteurs placés dans l'air. On peut faire l'expérience avec une bobine d'induction B (Fig. 1); les pôles du circuit induit P et P' sont reliés par des fils métalliques à deux micromètres à étincelles M et M' éloignés l'un de l'autre et offrant deux chemins distincts à peu près équivalents pour le passage de l'étincelle. On règle les micromètres de telle sorte que les étincelles passent à peu près aussi abondamment entre les boules de chacun d'eux. Quand on approche le radium de l'un des deux micromètres, les étincelles cessent de passer à travers l'autre.

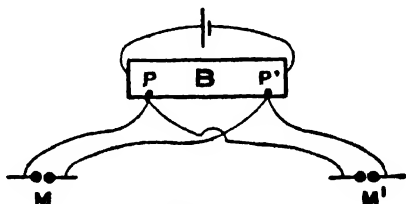


FIG 1

Les rayons les plus pénétrants semblent être les plus efficaces pour la production de ce phénomène; car, en faisant agir le radium au travers d'une plaque de plomb de 2 centimètres d'épaisseur, l'action sur l'étincelle n'est pas fortement diminuée, alors que la plus grande partie du rayonnement est arrêtée par la plaque.

## IV.

Les rayons du radium ne se réfléchissent pas, ne se réfractent pas. Ils forment un mélange hétérogène, et nous les diviserons en trois groupes, que nous désignerons par les lettres  $\alpha$ ,  $\beta$  et  $\gamma$  suivant la notation employée par Mr. Rutherford.

L'action d'un champ magnétique permet de les distinguer: dans un champ magnétique intense les rayons  $\alpha$  sont légèrement déviés de leur trajet rectiligne et cela de la même manière que les "rayons

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\* P. Curie, C.R. de l'ac. des sciences, 17 fév 1902



canaux" des tubes à vide, tandis que les rayons  $\beta$  sont déviés comme des rayons cathodiques, et que les rayons  $\gamma$  ne sont pas déviés et se comportent comme des rayons de Röntgen.\*

Le radium R (Fig. 2) est situé au fond d'une petite cavité cylindrique dans un bloc de plomb P. À l'abri de toute action magnétique, le rayonnement s'échappe de la cavité cylindrique sous la forme d'un pinceau rectiligne. Dans un champ magnétique uniforme normal au plan de la figure et dirigé vers l'arrière de ce plan, les

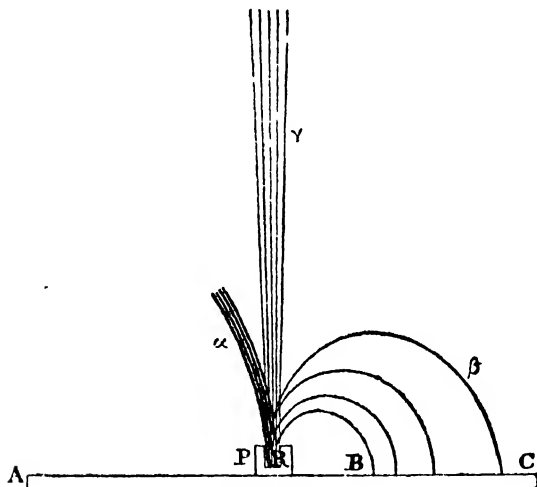


FIG. 2.

rayons  $\beta$  sont fortement déviés vers la droite et suivent un trajet circulaire, les rayons  $\alpha$  sont à peine déviés vers la gauche, les rayons  $\gamma$ , de beaucoup les moins intenses, continuent à s'échapper rectilignement.

Les rayons  $\alpha$  sont très peu pénétrants. Une lame d'aluminium de quelques centièmes de millimètres d'épaisseur les absorbent. Ces rayons ne sont que faiblement déviés par les champs magnétiques les plus intenses, et pour mettre en évidence cette déviation il faut en réalité employer un dispositif plus délicat que celui de la figure 2 qui n'est qu'une figure schématique.† On peut assimiler ces rayons à des projectiles dont la masse serait comparable à celle des atomes ;

\* *Giessel*, Wied. Ann., 2 nov. 1899. *Meyer et Von Schweidler*, Akad. Anzeig. Wien, 8 et 9 nov. 1899. *Becquerel*, C.R., 11 déc. 1899, 26 jan. et 16 fév. 1903. *P. Curie*, C.R., 8 jan. 1900. *Villard*, C.R. de l'ac., t. 130, p. 1010. *Rutherford*, Physik. Zeitsch., 15 jan. 1903.

† *Rutherford*, Phil. Mag., fév. 1903. *Becquerel*, C.R. de l'ac. des sciences, t. 136, p. 199.

ces projectiles seraient chargés d'électricité positive et se déplaceraient avec une grande vitesse. En dehors de l'action du champ magnétique, les lois de l'absorption des rayons  $\alpha$  par des écrans très minces superposés suffiraient pour caractériser ces rayons et en faire un groupe distinct.\* En traversant des écrans successifs les rayons  $\alpha$  deviennent en effet de moins en moins pénétrants (tandis que, dans les mêmes conditions, le pouvoir pénétrant des rayons de Röntgen va en augmentant). Il semble que l'énergie de chaque projectile diminue à la traversée de chaque écran.

Les rayons  $\alpha$  sont ceux qui semblent actifs dans la très belle expérience réalisée dans le *spinthariscopes* de Sir William Crookes. Dans cet appareil un fragment très petit d'un sel de radium (une fraction de milligramme) est maintenu par un fil métallique à une faible distance ( $\frac{1}{2}$  millimètre) d'un écran au sulfure de zinc phosphorescent. En examinant dans l'obscurité avec une loupe la face de l'écran qui est tournée vers le radium, on aperçoit des points lumineux parsemés sur l'écran et faisant songer à un ciel étoilé; ces points lumineux

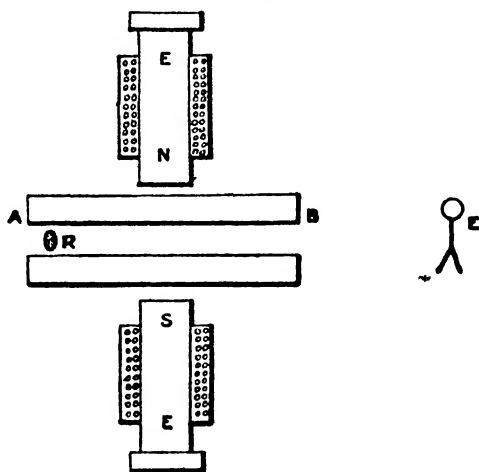


FIG. 3.

apparaissent et disparaissent continuellement. Dans la théorie balistique, on peut imaginer que chaque point lumineux qui apparaît résulte du choc d'un projectile. On aurait affaire pour la première fois à un phénomène permettant de distinguer l'action individuelle d'un atome.

Les rayons  $\beta$  sont analogues aux rayons cathodiques. Ils sont déviés par le champ magnétique de la même façon que ces derniers et

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\* *Mme. Curie*, C.R. de l'ac., 8 jan. 1900.

se comportent comme des projectiles chargés d'électricité négative qui s'échapperaient du radium avec une grande vitesse; ces projectiles (électrons) auraient une masse environ 1000 fois plus petite que celle d'un atome d'hydrogène. L'expérience suivante donne la démonstration de la déviation magnétique des rayons  $\beta$ . Une ampoule en verre renfermant un sel de radium R est placée à l'une des extrémités d'un tube de plomb à parois très épaisses A B (Fig. 8, coupe de l'appareil). On place un électroscope E un peu au delà de l'autre extrémité du tube. Le pinceau de rayons issus du radium et limité par le tube provoque la décharge de l'électroscope. Le tube de plomb est situé entre les branches d'un électroaimant E E et orienté normalement à la ligne des pôles N S. Quand le courant circule dans le fil de l'électroaimant, les rayons  $\beta$  sont rejetés sur les parois du tube de plomb; ils ne concourent plus à la décharge de l'électroscope, et cette décharge se fait lentement. Quand le courant est supprimé dans l'électroaimant, les rayons  $\beta$  agissent sur l'électroscope qui se décharge rapidement.

On peut prouver que les rayons  $\beta$  transportent de l'électricité négative, et ce résultat est en accord avec l'hypothèse dans laquelle on les considère comme des projectiles chargés d'électricité.\* On peut employer pour cela le dispositif expérimental de la Fig. 4; le radium R R émet des rayons  $\beta$ ; parmi ces rayons ceux qui s'échappent vers la partie supérieure traversent successivement une feuille mince d'aluminium E E E E reliée électriquement à la terre et une couche isolante de paraffine i i i i; ils sont ensuite absorbés par un bloc de plomb M M qui est réuni à un électromètre au moyen d'un fil métallique isole. On constate que le bloc de plomb M se charge continuellement d'électricité négative. Dans cette

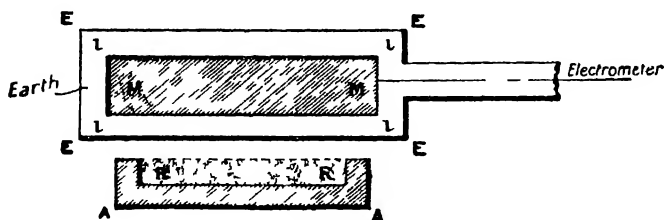


FIG. 4.

expérience les rayons  $\alpha$  sont absorbés par la feuille d'aluminium en relation avec la terre. La couche de paraffine est nécessaire pour obtenir un isolement convenable du bloc de plomb M M; cet isolement serait en effet tout à fait défectueux si le bloc de plomb était entouré d'air rendu conducteur par les rayons, et il serait alors

\* M et Mme Curie, C R de l'ac des sciences, 5 mars 1900.

impossible de constater à l'électromètre la charge électrique qui se dégage sur le morceau de plomb.

On peut faire l'expérience inverse : l'auge métallique A A (Fig. 5) est en relation avec l'électromètre et contient le radium R. Le tout est entouré de paraffine *iiii* et d'une enveloppe métallique E E E en relation électrique avec la terre. Les rayons  $\alpha$  très peu pénétrants

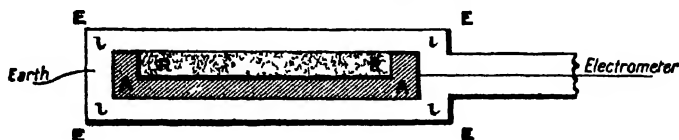


FIG. 5.

ne peuvent s'échapper ; les rayons  $\beta$  traversent la paraffine et emportent de l'électricité négative, pendant que l'auge métallique se charge positivement.

Une ampoule de verre scellée et contenant un sel de radium se charge spontanément d'électricité comme une bouteille de Leyde. Si au bout d'un temps suffisant on fait avec un couteau à verre un trait sur les parois de l'ampoule, il part une étincelle qui perce le verre en un point où la paroi est amincie sous le couteau ; en même temps l'opérateur éprouve une petite secousse dans les doigts, par suite du passage de la décharge.

Le groupe des rayons  $\beta$  est constitué par la réunion de rayons qui diffèrent les uns des autres par leur pouvoir pénétrant. Certains rayons  $\beta$  sont absorbés par une lame de  $\frac{1}{100}^{\text{me}}$  de millimètre d'épaisseur en aluminium, tandis que d'autres peuvent passer en se diffusant à travers une plaque de plomb de plusieurs millimètres d'épaisseur. On constate encore que les rayons  $\beta$  diffèrent les uns des autres par la courbure de la circonférence qu'ils décrivent dans un champ magnétique uniforme. Dans l'expérience représentée Fig. 2, les rayons  $\beta$  déviés par le champ magnétique impressionnent la plaque photographique A B C depuis B jusqu'en C. Les rayons les moins déviés impressionnent la plaque dans la région C, les rayons les plus déviés dans la région B. Sur la plaque on aura un véritable spectre produit par les rayons plus ou moins déviés séparés par le champ magnétique. En interposant une lame mince de métal sur le trajet des rayons contre la plaque photographique, on constate que les rayons les plus déviés sont supprimés. Les rayons les plus pénétrants sont donc les moins déviés.\*

Dans la théorie balistique on suppose que les rayons  $\beta$  sont formés par des électrons animés d'une vitesse plus ou moins grande. Les rayons les plus pénétrants sont ceux dont la vitesse est la plus grande. Les recherches de Kaufmann interprétées dans la théorie des électrons (sous la forme que lui a donnée Mr. Abraham) conduisent

\* Becquerel, C.R. de l'ac. des sciences, t. 130, pp. 206, 372, 810.

à des conclusions d'une grande importance générale :\* certains rayons  $\beta$  très pénétrants seraient constitués par des électrons animés d'une vitesse atteignant les  $\frac{1}{10}$ <sup>me</sup> de celle de la lumière ; la masse des électrons et peut-être celle de tous les corps serait la conséquence de réactions électromagnétiques ; l'énergie nécessaire pour donner à un corps chargé d'électricité une vitesse de plus en plus grande tendrait vers l'infini quand la vitesse du corps tendrait vers la vitesse de la lumière.

Les rayons  $\gamma$  non déviables et analogues aux rayons de Röntgen ne forment qu'une très faible partie du rayonnement total. Certains rayons  $\gamma$  sont extrêmement pénétrants et peuvent traverser plusieurs centimètres de plomb.

On peut utiliser les rayons de Becquerel pour faire des radiographies sans appareils spéciaux. Une petite ampoule en verre contenant quelques centigrammes d'un sel de radium remplace le tube de Crookes. On utilise les rayons  $\beta$  et  $\gamma$ . Les radiographies ainsi obtenues manquent de netteté par suite de la diffusion des rayons  $\beta$  par les corps qu'ils rencontrent. On obtient des radiographies bien nettes en faisant dévier les rayons  $\beta$  avec un électromagnét puissant et en utilisant seulement les rayons  $\gamma$  ; mais les rayons  $\gamma$  étant peu intenses, il faut alors plusieurs jours de pose pour obtenir une radiographie.

## V.

Les sels de radium dégagent continuellement de la chaleur.† Ce dégagement est assez fort pour qu'on puisse le montrer par une expérience grossière faite à l'aide

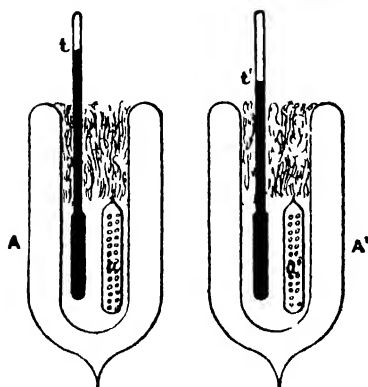


FIG. 6.

de deux thermomètres à mercure ordinaires. On utilise deux vases isolateurs thermiques à vide, identiques entr'eux (A et A', Fig. 6). Dans l'un de ces vases A on place une ampoule de verre *a* contenant 7 décigrammes de bromure de radium pur ; dans le deuxième vase A' on place une ampoule de verre *a'* qui contient une substance inactive quelconque, par exemple du chlorure de baryum. La température de chaque enceinte est indiquée par un thermomètre dont le réservoir est placé au voisinage immédiat de l'ampoule. L'ouverture

du coton. Dans ces conditions le thermomètre *t* qui se trouve dans le

\* Kaufmann, Nachrichten der k. Gesell. d. Wiss. zu Göttingen, 1901, Heft 2 ; C.R. de l'ac. des sciences, 13 oct. 1902.

† Curie et Laborde C.R. de l'ac. des sciences, 16 mars 1903.

même vase que le radium, indique constamment une température supérieure de  $3^{\circ}$  à celle indiquée par l'autre thermomètre *t'*.

On peut évaluer la quantité de chaleur dégagée par le radium à l'aide du calorimètre à glace de Bunsen. En plaçant dans ce calorimètre une ampoule de verre qui contient le sel de radium, on constate un apport continu de chaleur qui s'arrête dès que l'on éloigne le radium. La mesure faite avec un sel de radium préparé depuis longtemps indique que chaque gramme de radium dégage environ 80 petites calories pendant chaque heure. Le radium dégage donc pendant chaque heure une quantité de chaleur suffisante pour fondre son poids de glace. Cependant le sel de radium utilisé semble toujours rester dans le même état et, du reste, aucune réaction chimique ordinaire ne pourrait être invoquée pour expliquer un pareil dégagement continu de chaleur.

On constate encore qu'un sel de radium qui vient d'être préparé dégage une quantité de chaleur relativement faible. La chaleur dégagée en un temps donné augmente ensuite continuellement et tend vers une valeur déterminée qui n'est pas encore tout à fait atteinte au bout d'un mois.

Quand on dissout dans l'eau un sel de radium et que l'on enferme la solution dans un tube scellé, la quantité de chaleur dégagée par la solution est d'abord faible; elle augmente ensuite et tend à devenir constante au bout d'un mois. Quand l'état limite est atteint le sel de radium enfermé en tube scellé dégage la même quantité de chaleur à l'état solide et à l'état de dissolution.

On peut encore évaluer la chaleur dégagée par le radium à diverses températures, en l'utilisant pour faire bouillir un gaz liquéfié et en mesurant le volume du gaz qui se dégage. On peut faire l'expérience avec le chlorure de méthyle (à  $-21^{\circ}$ ). L'expérience a été faite aussi par Mr. le professeur Dewar et Mr. Curie avec l'oxygène liquide (à  $-180^{\circ}$ ) et l'hydrogène liquide (à  $-292^{\circ}$ ). Ce dernier corps convient particulièrement bien pour réaliser l'expérience: un tube A, Fig. 7 (fermé à la partie inférieure et entouré d'un isolateur thermique à vide de Dewar), contient un peu d'hydrogène liquide H; un tube de dégagement *tt* permet de recueillir le gaz dans une éprouvette graduée E remplie d'eau. Le tube A et son isolateur plongent tous deux dans un bain d'hydrogène liquide H'. Dans ces conditions aucun dégagement gazeux ne se produit dans le tube A. Lorsque l'on place une ampoule *a* contenant 7 décigrammes de bromure de radium dans l'hydrogène du tube A, il se fait un dégagement continu de gaz hydrogène, et l'on recueille 73 centimètres cubes de gaz par minute.

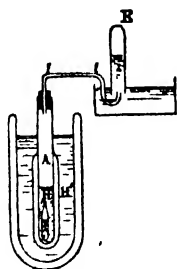


FIG. 7.

## VI.

Les rayons du radium provoquent diverses actions chimiques. Ils agissent sur les substances employées en photographie de la même façon que la lumière. Ils colorent le verre en violet ou en brun, les sels alcalins en jaune, en violet, en bleu ou en vert. Sous leur action la paraffine, le papier, le celluloid jaunissent, le papier devient cassant, le phosphore ordinaire se transforme en phosphore rouge. D'une manière générale, les corps qui sont phosphorescents sous l'action des rayons du radium, subissent une transformation, et en même temps leur pouvoir phosphorescent tend à disparaître. Enfin, dans le voisinage des sels de radium on peut constater dans l'air la production d'ozone.

## VII.

Les rayons du radium provoquent diverses actions physiologiques.

Un sel de radium, situé dans une boîte opaque en carton ou en métal, agit cependant sur l'œil et donne une sensation de lumière. Pour obtenir ce résultat on peut placer la boîte contenant le radium devant l'œil fermé ou contre la tempe. Dans ces expériences les milieux de l'œil deviennent lumineux par phosphorescence sous l'influence des rayons du radium et la lumière que l'on aperçoit a sa source dans l'œil lui-même.\*

Les rayons du radium agissent sur l'épiderme; si on tient pendant quelques minutes une ampoule contenant du radium sur la peau, on n'éprouve aucune sensation particulière, mais, 15 à 20 jours après, il se produit sur la peau une rougeur, puis une escharre dans la région où a été appliquée l'ampoule; si l'action du radium a été assez longue, il se forme ensuite une plaie qui peut mettre plusieurs mois à guérir. L'action des rayons du radium sur l'épiderme est analogue à celle produite par les rayons de Rontgen. On essaye actuellement d'utiliser cette action dans le traitement des lupus et des cancers.†

Les rayons du radium agissent encore sur les centres nerveux et déterminent alors des paralysies et la mort. Ils semblent aussi agir d'une façon particulièrement intense sur les tissus vivants en voie d'évolution.‡

## VIII.

Lorsque l'on place un corps solide quelconque dans le voisinage d'un sel de radium, on constate que ce corps acquiert les propriétés radiantes du radium; il devient radio-actif. Cette radio-activité

\* *Giesel*, Naturforscherversammlung Munchen, 1899. *Himstedt et Nagel*, Ann. der Physik, t. 4, 1901.

† *Walkhoff*, Phot. Rundschau, oct. 1900. *Giesel*, Berichte d. deutsch. chem. Gesell., t. 23. *Becquerel et Curie*, C.R. de l'ac., t. 132, p. 1289.

‡ *Danysz*, C.R. de l'ac. des sciences, 16 fev. 1903. *U. Bohn*, C.R. de l'ac. des sciences, 27 avril 1903.

*induite* persiste encore un certain temps quand on éloigne le corps du radium, cependant elle s'affaiblit progressivement, elle diminue de moitié environ pendant chaque demi-heure et finit par s'éteindre.

Ce phénomène se produit d'une façon régulière et particulièrement intense si l'on enferme les corps avec un sel de radium dans une enceinte close. Il y a aussi grand avantage à placer dans l'enceinte une solution d'un sel de radium plutôt que le sel solide.\*

Une solution d'un sel de radium est située en A, Fig. 8, dans un réservoir en verre qui communique par les tubes *t* et *t'* avec deux autres réservoirs en verre remplis d'air B et C. On constate que les parois des réservoirs B et C sont radio-actifs, ils émettent des rayons de Becquerel analogues à ceux émis d'ordinaire par le radium lui-même, tandis que, au contraire, la solution du sel de radium émet très peu de rayons, la radio-activité est en quelque sorte extériorisée.

Les phénomènes qui viennent d'être décrits se produisent aussi bien dans un autre gaz que l'air et cela quelle que soit la pression du gaz. La radio-activité se communique de proche en proche par une sorte de conduction à travers les gaz; elle peut même se propager d'un réservoir à un autre par un tube capillaire. Le gaz qui a séjourné près du radium a donc acquis la propriété de rendre les corps solides radio-actifs, le gaz lui-même est du reste radio-actif mais il n'émet que des rayons très peu pénétrants. (Les rayons émis par le gaz ne peuvent pas traverser les parois d'un réservoir en verre.) Lorsque le gaz ainsi modifié est entraîné loin du radium, il conserve assez longtemps ses propriétés; il continue à émettre des rayons de Becquerel très peu pénétrants et à provoquer la radio-activité des corps solides. Son activité à ce double point de vue diminue cependant de moitié pendant chaque période de quatre jours et finit par s'éteindre.

Mr. Rutherford suppose que le radium dégage constamment une substance gazeuse radio-active qui se répand dans l'espace et provoque les phénomènes de la radio-activité induite. Il donne à cette substance hypothétique le nom d'*émanation du radium* et pense qu'elle se trouve à l'état de mélange dans les gaz qui ont séjourné dans le voisinage du radium. Sans admettre nécessairement la nature matérielle de l'émanation, on peut employer cette expression pour désigner l'énergie radio-active de forme spéciale emmagasinée dans le gaz.†

L'air chargé d'émanation provoque la phosphorescence des corps

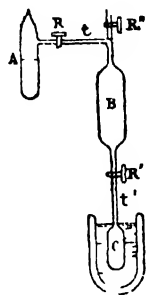


FIG 8

\* Mr. et Mme. Curie, C R de l'ac des sciences, 6 nov. 1899. Curie et Debierne, C R de l'ac. des sciences, 4 mars 1901, 29 juillet 1901, 25 mars 1901.

† Rutherford, Phil Mag, 1900, 1901, 1902, plusieurs mémoires. Dorn, Abh. Naturforschgesell. Halle, juin 1900. P. Curie, C R de l'ac. des sciences, 17 nov. 1902, 26 jan. 1903



qui se trouvent en sa présence ; le verre (plus particulièrement le verre de Thuringe) donne une belle phosphorescence blanche ou verte. Le sulfure de zinc de Sidot devient excessivement brillant sous l'action de l'émanation.\* On peut faire l'expérience avec l'appareil représenté Fig. 8. Le robinet R étant fermé l'émanation radio-active qui se dégage de la solution de sel de radium en A se répand dans l'air au-dessus de la solution. Lorsque l'émanation s'est ainsi accumulée en A pendant quelques jours, on fait le vide dans les réservoirs B et C, dont les parois intérieures sont enduites de sulfure de zinc phosphorescent. On ferme ensuite le robinet R', et on ouvre le robinet R. L'air chargé d'émanation est alors aspiré brusquement dans les réservoirs B et C qui deviennent aussitôt lumineux.

L'émanation du radium se comporte comme un gaz à bien des points de vue : elle se partage comme un gaz entre deux réservoirs qui communiquent entre eux. Elle se diffuse dans l'air suivant la loi de diffusion des gaz et possède un coefficient de diffusion voisin de celui de l'acide carbonique dans l'air.†

Mrs. Rutherford et Soddy ont découvert que l'émanation a la propriété de se condenser à la température de l'air liquide.‡ On peut montrer les effets de cette condensation en faisant encore usage de l'appareil représenté Fig. 8. Le robinet R' étant fermé et l'émanation étant répandue dans tout l'appareil comme à la fin de l'expérience précédemment décrite, les réservoirs B et C (couverts intérieurement d'une couche de sulfure de zinc de Sidot) sont lumineux. On ferme alors le robinet R et on plonge le réservoir C dans l'air liquide. Au bout d'une demi-heure, on constate que le réservoir B a perdu toute sa luminosité, tandis que le réservoir C est encore lumineux. L'émanation a en effet quitté le réservoir B et est venue se condenser en C dans la partie refroidie. Cependant le réservoir C n'est pas très lumineux, parce que la phosphorescence du sulfure du zinc est plus faible à la température de l'air liquide qu'à la température ambiante. On ferme ensuite le robinet R', ce qui interrompt la communication entre les deux réservoirs B et C, on retire le réservoir C de l'air liquide et on le laisse revenir à la température ambiante. Le réservoir C est alors vivement illuminé tandis que le réservoir B est toujours obscur ; l'émanation qui, au début de l'expérience, était répandue dans les deux réservoirs se trouve en effet, tout entière, maintenant dans le réservoir C.

Les expériences précédentes conduisent à assimiler l'émanation à un gaz analogue à un gaz matériel. Cependant, jusqu'ici, l'hypothèse de l'existence d'un pareil gaz est uniquement basée sur des manifestations radio-actives. Remarquons encore que, contrairement à ce qui se passe pour la matière ordinaire, l'émanation disparaît spon-

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\* Curie et Debierne, C.R. de l'ac, 2 déc. 1901.

† Curie et Danne, C.R. de l'ac. des sciences, 1903. Rutherford et Miss Brookes, Chemical News, 1902, 29 avril.

‡ Rutherford et Soddy, Phil. Mag, mai 1903.

tanément dans un tube scellé qui la renferme ; la quantité d'émanation diminue de moitié en quatre jours, et cette constante de temps est une donnée caractéristique de l'émanation du radium.

## IX.

Après avoir énuméré les propriétés principales du radium, il convient de rappeler brièvement l'origine de sa découverte à laquelle Mme. Curie a pris une très grande part.\*

L'étude des corps renfermant de l'uranium et du thorium avait montré que *la radio-activité est une propriété atomique* qui accompagne partout l'atome de ces deux corps simples ; la radio-activité d'une substance composée est en général d'autant plus forte, que la proportion du métal radio-actif contenue dans cette substance est elle-même plus grande. Certains minéraux d'uranium : la pechblende, la chalcocite, la carnotite, ont, cependant, une radio-activité plus forte que celle de l'uranium métallique. Nous nous sommes demandés si ces minéraux ne renfermaient pas, en petite proportion, quelques substances encore inconnues et fortement radio-actives, et nous avons recherché ces substances hypothétiques par les voies de l'analyse chimique, en nous guidant constamment par la radio-activité des matières traitées. Nos prévisions ont été vérifiées par l'expérience ; la pechblende contient des substances radio-actives nouvelles, mais ces substances sont dans le minerai dans une proportion excessivement faibles. Une tonne de pechblende, par exemple, contient une quantité de radium de l'ordre de grandeur de 1 décigramme. Dans ces conditions la préparation des sels de radium est pénible et coûteuse. Une tonne de minerai fournit quelques kilogrammes de bromure de baryum radifère, d'où l'on extrait ensuite le bromure de radium par une série de fractionnements.

Pendant la séparation du radium, Demarçay dont nous avons à déplorer la mort récente, a bien voulu examiner les spectres des produits que nous avions préparés. Ce concours nous a été précieux ; dès le début de nos recherches, l'analyse spectrale est venue confirmer nos prévisions, en nous apportant la preuve que le baryum radio-actif que nous avions retiré de la pechblende contenait un élément nouveau. C'est à Demarçay que nous devons la première étude du spectre du radium.†

Le radium a une réaction spectrale très sensible, aussi sensible que celle du baryum, on peut reconnaître au spectroscopie la présence du radium dans un sel de baryum radifère qui ne contient que  $\frac{1}{10000}$  de radium. Mais la radio-activité du radium donne une réaction 10,000 fois plus sensible encore. Un électromètre ordinaire bien isolé permet de déceler facilement la présence du radium lorsqu'il est mélangé à des substances inactives dans la proportion de  $\frac{1}{10^5}$ .

\* Mme. Curie, Thèse à la Faculté des sciences, Paris, 1903.

† Demarçay, C.R. de l'ac. des sciences, déc. 1898 et juillet 1900.

Le radium est l'homologue supérieur du baryum dans la série des métaux alcalino-terreux ; son poids atomique égal à 225 a été déterminé par Mme Curie.

Bien que cet élément soit très voisin du baryum, il ne s'en trouve pas, même à l'état de trace, dans les minerais ordinaires de baryum. Le radium n'accompagne le baryum que dans les minerais d'urane, et ce fait a probablement une grande importance théorique.

## X.

Le radium nous donne l'exemple d'un corps qui, tout en conservant le même état, donne lieu à un dégagement d'énergie continu et assez considérable. Ce fait paraît en désaccord avec les principes fondamentaux de l'énergétique et diverses hypothèses ont été proposées pour éviter cette contradiction.

Parmi ces hypothèses nous en retiendrons deux qui ont été émises dès le début des études sur la radio-activité.\*

Dans la première hypothèse, on suppose que le radium est un élément en voie d'évolution. On doit alors admettre que cette évolution est extrêmement lente de telle sorte qu'aucun changement d'état appréciable ne se fait sentir au bout de plusieurs années. L'énergie que le radium dégage pendant une année correspondrait donc à une transformation insignifiante de ce corps. Il semble d'ailleurs naturel de supposer que la quantité d'énergie mise en jeu dans la transformation des atomes est considérable.

La deuxième hypothèse consiste à supposer qu'il existe dans l'espace des rayonnements encore inconnues et inaccessibles à nos sens. Le radium serait capable d'absorber l'énergie de ces rayons hypothétiques et de la transformer en énergie radio-active.

Les deux hypothèses que nous venons énoncer ne sont pas du reste incompatibles.

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\* *Mme. Curie*, Revue générale des sciences, 30 jan 1899

Friday, January 15, 1904.

SIR BENJAMIN BAKER, K.C.B. K.C.M.G. LL.D. F.R.S. M.Inst.C.E.,  
Vice-President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, O.M. M.A. D.C.L. LL.D. Sc.D.  
F.R.S. *M.R.I.*, Professor of Natural Philosophy, R.I.

*Shadows.*

My subject is shadows, in the literal sense of the word—shadows thrown by light, and shadows thrown by sound. The ordinary shadow thrown by light is familiar to all. When a fairly large obstacle is placed between a small source of light and a white screen, a well-defined shadow of the obstacle is thrown on the screen. This is a simple consequence of the approximately rectilinear path of light. Optical shadows may be thrown over great distances, if the light is of sufficient intensity: in a lunar eclipse the shadow of the earth is thrown on the moon: in a solar eclipse the shadow of the moon is thrown on the earth. Acoustic shadows, or shadows thrown by sound, are not so familiar to most people; they are less perfect than optical shadows, although their imperfections are usually over-estimated in ordinary observations. The ear is able to adjust its sensitiveness over a wide range, so that, unless an acoustic shadow is very complete, it often escapes detection by the unaided ear, the sound being sufficiently well heard in all positions. In certain circumstances, however, acoustic shadows may be very pronounced, and capable of easy observation.

The difference between acoustic and optical shadows was considered of so much importance by Newton, that it prevented him from accepting the wave theory of light. How, he argued, can light and sound be essentially similar in their physical characteristics, when light casts definite shadows, while sound shadows are imperfect or non-existent? This difficulty disappears when due weight is given to the consideration that the lengths of light waves and sound waves are of different orders of magnitude. Visible light consists of waves of which the average length is about one forty-thousandth of an inch. Audible sound consists of waves ranging in length from about an inch to nearly forty feet: the wave length corresponding to the middle C of the musical scale is roughly equal to four feet. It is, therefore, no matter for wonder that the effects produced by sound waves and by light waves differ in important particulars.

Moreover, the wave length is not the only magnitude on which the perfection of the shadow depends; the size of the obstacle, and the

distance across which the shadow is thrown, must also be taken into consideration. The optical shadow of a small object, thrown across a considerable distance, partakes of the imperfections generally observed in connection with sound shadows.

It was calculated by the French mathematician, Poisson, that, according to the wave theory of light, there should be a bright spot in the middle of the shadow of a small circular disc—a result that was thought to disprove the wave theory by a *reductio ad absurdum*. Although unknown to Poisson, this very phenomenon had actually been observed some years earlier, and was easily verified when a suitably arranged experiment was made.

Under suitable conditions a bright spot can be observed at the centre of the shadow of a three-penny bit. The coin may be supported by three or four very fine wires, and its shadow thrown by

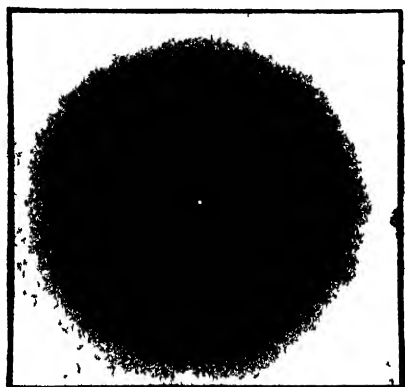


FIG. 1.—REPRODUCTION OF A PHOTOGRAPH OF THE SHADOW OF A SILVER PENNY PIECE.

sunlight admitted at a pin-hole aperture placed in the shutter of a darkened room. The coin may be at a distance of about fifteen feet from the aperture, and the screen at about fifteen feet beyond the coin. To obtain a more convenient illumination, a larger aperture in the shutter may be filled by a short focus lens, which forms a diminutive image of the sun, this image serves as a point source of light. A smaller disc has some advantages. Fig. 1 is reproduced from a photograph of the shadow of a silver penny piece, struck at the time of the Coronation. The shadow, formed in the manner just described, was allowed to fall directly on a photographic plate; after development a negative was obtained, in which the dark parts of the shadow were represented by transparent gelatine, while the bright parts were represented by opaque deposits of silver. To obtain a correct representation, a contact print was formed from the negative in the usual

way, upon a lantern plate; and from this Fig. 1 has been reproduced.

It is at once evident that at the centre of the shadow, where one would expect the darkness to be most complete, there is a distinct bright spot. This result has always been considered a valuable confirmation of the wave theory of light.

I now propose to speak of acoustic shadows—shadows thrown by sound. The most suitable source of sound for the following experiments is the bird-call,\* which emits a note of high pitch—so high, indeed, that it is inaudible to most elderly people. The sound emitted has two characteristics, valuable for our purpose—the wave length is very short; and the sound is thrown forward, without too much tendency to spread, thus differing from sounds produced by most other means.

Since the sound emitted is nearly inaudible, some objective method of observing it is required. For this purpose we may utilise the discovery of Barrett and Tyndall, that a gas flame issuing under somewhat high pressure from a pin-hole burner *flares* when sound waves impinge on it, but recovers and burns steadily when the sound ceases. The sensitiveness of the flame depends on the pressure of the gas, which should be adjusted so that flaring just does not occur in the absence of sound. If the bird-call is directed towards the sensitive flame, the latter flares so long as the call is sounded and no obstacle intervenes. On interposing the hand about midway between the two, the flame recovers and burns steadily. Thus the sound emitted by the bird-call casts a shadow, and to this extent resembles light.

It will now be shown that the sensitive flame flares when it is placed at the centre of the acoustic shadow thrown from a circular disc, but recovers in any other position within the shadow; thus proving that there is sound at the centre of the shadow, although at a small distance from this point there is silence. The part of the flame which is sensitive to sound is that just above the pin-hole orifice, so that it is necessary to arrange the bird-call, the centre of the disc, and the pin-hole orifice in a straight line. For the disc, it is convenient to use a circular plate of glass about 18 inches in diameter with a piece of black paper pasted over its middle portion, a small hole being cut in the *paper* exactly at the centre of the disc. The glass disc is hung by two wires, and the positions of the bird-call and sensitive flame can be adjusted by sighting through the hole in the paper. If the disc is caused to oscillate in its own plane, the flame flares every time that the disc passes through its position of equilibrium, and recovers whenever the disc is not in that position. The analogy between this experiment, and that in which a bright spot is formed at the centre of the optical shadow of a small disc, is sufficiently obvious.

The approximate theory of the shadow of the circular disc is

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\* See 'Proc Roy. Inst,' Jan. 17, 1902.

easily given, and it explains the leading features of the phenomenon. But, even in the simpler case of sound, an exact calculation which shall take full account of the conditions to be satisfied at the edge, has so far baffled the efforts of mathematicians. When the obstacle is a sphere, the problem is more tractable, and, in a recent memoir in the 'Philosophical Transactions' a solution is given, embracing the cases where the circumference of the sphere is as great as two or even ten wave-lengths. When the sphere is small relatively to the wave-length, the calculation is easy, but the difficulty rapidly increases as the diameter rises. The diagram gives the intensity in various positions on the surface of the sphere when plane waves of sound, i.e. waves proceeding from a distant source, impinge upon it. The intensity is a maximum at the point  $0^\circ$  nearest to the source, which may be called the pole. From the pole to the equator, distant  $90^\circ$  from it, the intensity falls off, and the fall continues as we enter the hinder hemisphere. But at an angular distance from the pole of about  $135^\circ$  in one case and  $165^\circ$  in the other, the intensity reaches a minimum and thence increases towards the antipole at  $180^\circ$ .

In private experiments the distribution of sound over the surface of the sphere may be explored with the aid of a small Helmholtz resonator and a flexible tube, and in this way evidence may be obtained of the rise of sound in the neighbourhood of the antipole. A more satisfactory demonstration is obtained by the method already employed in the case of the disc, the disc being replaced by a globe (about 12 inches in diameter), or by a croquet-ball of about  $3\frac{1}{2}$  inches diameter. In the former case the burner may be situated behind the sphere at such a distance as 5 inches. In the latter a distance of  $1\frac{1}{2}$  inches (from the surface) suffices. By a suitable adjustment of the flame, flaring ensues when everything is exactly in line, but the flame recovers when the ball is displaced slightly in a transverse direction. Since the wave-length of the sound is 3 cm. and the circumference of the croquet-ball is about 30 cm, this case corresponds to the curve B of our diagram.

In connection with the mathematical investigation which led to the results represented graphically in Fig. 2, there is a point of interest which I should like to mention. The investigation was carried out upon the supposition that the source of sound is at a considerable distance, so that the waves reaching the sphere are plane; and that the receiver, by which the sound is detected, is situated on the surface of the sphere. At any given position on the surface of the sphere, the receiver will indicate the reception of sound of a certain intensity, which may be read off from Fig. 2. Now the final results assume a form which shows that, if the positions of the source and the receiver are interchanged, the latter will indicate the reception of sound of the same intensity as in the original arrangement. Thus each of the curves in Fig. 2 represents the solution of two distinct problems: the intensity of the sound derived from a distant source

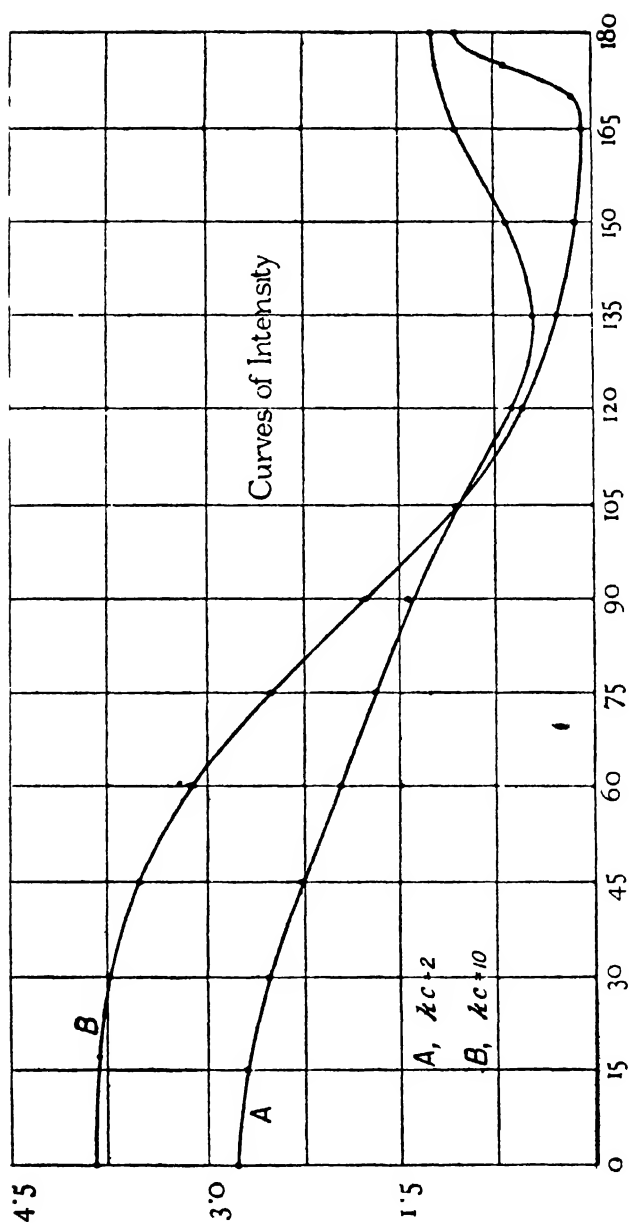


FIG. 2.



and detected at any point on the surface of the sphere; and the intensity of the sound derived from a source on the surface of the sphere, and observed at a distant point. This result forms an interesting example of a principle of very wide application, which I have termed the *Principle of Reciprocity*. Some special cases were given many years ago by Helmholtz.

It is a matter of common observation that if one person can see another, either directly or by means of any number of reflections in mirrors, then the second person can equally well see the first. The same law applies to hearing, apparent exceptions being easily explained. For instance, such is the case of a lady sitting in a closed carriage, listening to a gentleman talking to her through the open window. If the street is noisy, the lady can hear what the gentleman says very much more distinctly than he can hear what she replies. This is due to the fact that the gentleman's ears are assailed by noises of the street from which the lady's ears are shielded by the walls of the carriage.

Another instance may be mentioned, which will appeal to electricians. In the arrangement known as Wheatstone's bridge, resistances are joined in the form of a lozenge, a galvanometer being connected between two opposite angles of the lozenge, while a battery is connected between the other two angles. When the resistances are suitably adjusted, no current flows through the galvanometer; but a slight want of adjustment produces a deflection of the galvanometer, thus indicating the passage of a small current. Now, if the positions of the battery and the galvanometer are interchanged, without alteration of resistance, the same current as before will flow through the galvanometer, and therefore the deflection will be the same as before. Thus with a given cell, galvanometer and set of resistances, the sensitiveness of the Wheatstone's bridge arrangement is the same whichever pair of opposite angles of the lozenge are joined by the galvanometer. If a source of alternating E.M.F. is used instead of the battery, and a telephone is substituted for the galvanometer, then the principle of reciprocity still applies, whether the resistances are inductive or non-inductive.

A simple illustration, of a mechanical nature, is now shown. Fig. 3 represents a straightened piece of watch-spring clamped at one end to a firm support. A weight can be hung at either of the points A or B of the spring, when it may be observed that the deflection at B due to the suspension of the weight at A, is exactly equal to the deflection at A due to the suspension of the weight at B. This result is equally true wherever the points A and B may be situated; it applies not only to a loaded spring, which has been chosen as suitable for a simple lantern demonstration, but also to any sort of beam or girder.

It will have become clear, from what has been said, that waves encounter considerable difficulty in passing round the outside of a curved surface. I wish now to refer to a complementary pheno-

menon—the ease with which waves travel round the *inside* of a curved surface. This is the case of the whispering gallery, of which there is a good example in St. Paul's Cathedral. The late Sir George Airy considered that the effect could be explained as an instance of concentrated echo, the sound being concentrated by the curved walls, just as light may be brought to a focus by a concave mirror. From

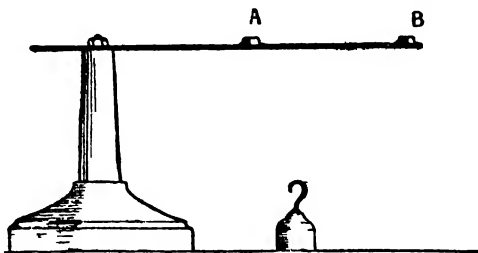


FIG. 3.—TO ILLUSTRATE A SIMPLE MECHANICAL APPLICATION OF THE PRINCIPLE OF RECIPROCITY.

my own observations, made in St. Paul's Cathedral, I think that Airy's explanation is not the true one; for it is not necessary, in order to observe the effect, that the whisperer and the listener should occupy particular positions in the gallery. Any positions will do equally well. Again, whispering is heard more distinctly than ordinary conversation, especially if the whisperer's face is directed

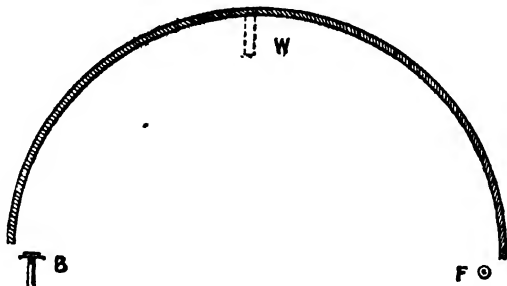


FIG. 4.—MODEL ILLUSTRATING THE PECULIARITIES OF A WHISPERING GALLERY.

along the gallery towards the listener. It is known that a whisper has less tendency to spread than the full-spoken voice; thus a whisper, heard easily in front of the whisperer, is inaudible behind that person's head. These considerations led me to form a fairly satisfactory theory of the whispering gallery, nearly twenty-five years ago.\* The phenomenon may be illustrated experimentally

\* 'Theory of Sound,' § 287.

by the small scale arrangement represented diagrammatically in Fig. 4. A strip of zinc, about 2 feet wide and 12 feet long, is bent into the form of a semicircle; this forms the model of the whispering gallery. The bird-call B is adjusted so that it throws the sound tangentially against the inner surface of the zinc: it thus takes the place of the whisperer. The sensitive flame F takes the place of the listener. A flame is always more sensitive to sound reaching it in one direction than in others; the flame F is therefore adjusted so that it is sensitive to sounds leaving the gallery tangentially. The flaring of the flame shows that sound is reaching it: if an obstacle is interposed in the straight line F B the flame flares as before; but if a lath of wood W, which need not be more than 2 inches wide, is placed against the inner surface of the zinc, the flame recovers, showing that the sound has been intercepted. Thus the sound creeps round the inside surface of the zinc, and there is no disturbance except at points within a limited distance from that surface.

[R.]

Friday, February 19, 1904,

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

C. T. R. WILSON, Esq., M.A. F.R.S.,  
Fellow of Sidney Sussex College, Cambridge.

*Condensation Nuclei.*

A FAMILIAR experiment was first shown illustrating the action of ordinary dust particles as condensation nuclei. From a large globe, which had been allowed to stand for some hours, some of the air was removed by opening communication with an exhausted vessel. Only a very few drops were formed as a result of the expansion. On allowing air to enter the globe through a cotton-wool filter, so that the pressure was brought back to its original value (that of the atmosphere), and allowing the air to expand as before, the drops formed were again very few. The ordinary air of the room was now admitted; an expansion of the air in this case resulted in the production of a thick fog.

When air has been freed from dust by filtering, or by repeatedly forming a cloud by expansion, and allowing it to settle, the vapour which, in the presence of the nuclei would have separated out in drops, must be in the "supersaturated" condition immediately after the expansion is completed.

Another method of producing clouds was now shown. Air was allowed to escape through a fine orifice into an atmosphere of steam; the mixed air and steam were then passed through a Liebig's condenser, where the greater part of the steam was condensed, and then into a large glass globe, where the clouds were observed. From this vessel the air was drawn off by a pump which maintained the pressure in the globe and condenser at a considerable number of cms. of mercury below that of the atmosphere. Before reaching the jet the air of the room had to pass through a cotton-wool filter, and then through a long tube containing water; finally it was led through an aluminium tube to the orifice. The latter was about half a mm. wide. The fall of pressure in passing through the orifice was about 15 or 20 cms. In the absence of the filter, the air being admitted directly to the water tube through a tap turned just sufficiently to give the same flow as with the filter, a dense fog poured out from the end of the condenser tube; on closing the tap and letting the air

enter through the filter the fog rapidly cleared, and only a fine rain continued to be produced. While the apparatus was in this condition an X-ray tube was set in action near the aluminium tube; the rain was succeeded by fog, which continued to pour out from the end of the condenser so long as the X-rays were kept in action. Condensation nuclei are, as this experiment proves, produced in air exposed to Rontgen rays. Later experiments will, however, show that they have entirely different properties from the ordinary dust nuclei.

When air has been completely freed from dust particles, so that a slight expansion of the air (initially saturated with water vapour) does not result in the formation of any drops, it is found that quite a high degree of supersaturation may be brought about without the appearance of a single drop. There is, however, a limit to the supersaturation which can exist without condensation of the vapour in drops resulting. To study this condensation in dust-free air, and to measure the expansion required to produce the necessary degree of supersaturation, a special form of expansion apparatus is required. The lantern slide thrown on the screen shows the construction and mode of working of the apparatus. The second slide is a photograph of the machine in action, the exposure having been made immediately after an expansion; the cloud formed (in this case on nuclei produced by the action of radium) is plainly visible along the path of a concentrated beam of light from a lantern.

Let us now try an actual experiment with the expansion apparatus. On making a slight expansion a cloud forms on the dust particles which are present; this slowly settles to the bottom of the vessel. The air is allowed to contract to its original volume, and a second expansion of the same amount made. The drops formed are on this occasion comparatively few, and they fall rapidly; the dust particles have nearly all been carried down with the drops formed by the previous expansion. The fewer the nuclei on which water condenses the larger will be the share of water available for each drop, and the more rapid will be the fall. The next expansion produces no drops. While the air is in the expanded condition, the piston being at the bottom of the expansion cylinder, air is removed from the cloud chamber by opening the connexion to the air-pump until the pressure is about 13 or 14 cms. of mercury below that of the atmosphere; the piston is again allowed to rise by putting the air space below it in communication with the atmosphere. The next expansion is thus comparatively large, the pressure after the expansion has taken place and the temperature has risen to its original value being 13 cms. or more below the initial pressure. Yet, in spite of the high degree of supersaturation reached, not a drop of water is seen. Making the fall of pressure 16 cms., however, we see on expansion a shower of drops. And although these drops are few and large, falling therefore rapidly, yet, however often the same expansion be repeated, the drops produced on expansion show no diminution in number. Thus the nuclei removed with the drops are

continually replaced by others manufactured within the apparatus itself.

To produce the necessary supersaturation to cause condensation in the form of drops in dust-free air, the air must be allowed to expand suddenly till the final volume is 1.25 times the initial volume. The condensation is rain-like in form, and moreover the number of drops remains small although the expansion considerably exceeds this lower limit. Expansions exceeding the limit,  $v_2/v_1 = 1.38$ , however, give fogs, which increase rapidly in density, i.e. in the number of the drops, as the expansion is increased beyond this second limit. The expansions required for the rain-like and cloud-like condensations correspond to a fourfold and eightfold supersaturation respectively.

A further experiment will throw light on the nature of the nuclei associated with the rain-like condensation. Let us expose the moist air to the action of X-rays before causing it to expand. First let us try an expansion very slightly less than that required to give the rain-like condensation without the rays. You observe, no drops are formed. Now let the expansion be slightly greater than the critical value, 1.25. A fog is seen on expansion. Thus the X-rays produce in the air immense numbers of nuclei having the same properties, so far as their power of assisting condensation goes, as the comparatively few nuclei which the rain-like condensation makes visible. Now, a gas exposed to X-rays conducts electricity, and the otherwise complicated phenomena of this conduction are all reduced to comparative simplicity by the theory that under the action of the rays equal numbers of freely moving positively and negatively electrified bodies (the ions) are produced from the originally neutral gas. It is at once suggested that the condensation nuclei produced by X-rays are simply these ions.

Let us now impart conducting power to the gas by exposing it to the action of the radiation from radium. Again we have the same result, no drops produced if the expansion be less than 1.25, fog if the expansion exceed this limit.

If we substitute for the glass shade, which has thus far formed the cloud-chamber, a glass cylinder with a horizontal metal top, we have the means of testing whether the condensation nuclei produced by Röntgen or radium rays are really electrically charged, whether in fact it is the ions themselves which act as condensation nuclei or other particles produced by the rays. If, for example, the roof of the cloud chamber be kept positively charged and the floor negatively, the negatively charged ions will travel upwards and the positively charged ones downwards. In the absence of an electric field the positive and negative ions produced by the action of the rays will go on increasing in number until as many are neutralised by recombination with ions of the opposite kind, or by coming in contact with the walls of the vessel, in each second, as are set free in that time by the rays. If the rays be cut off, the removal of ions by recom-

bination and diffusion will continue, and the number of ions in the vessel will diminish rapidly.

Experiment shows that, while in the absence of an electric field, quite a considerable fog is formed when an expansion, slightly exceeding 1.25, is effected 10 seconds after the rays have been cut off, with 200 volts between the upper and lower plates the same expansion, allowed to take place 3 or 4 seconds after the stopping of the rays, produces only a very slight shower. Or, again, if the rays be kept on all the time the resulting fog is very much less dense with the electric field acting than without it. These results are easily explained if we assume that the condensation nuclei are the ions, and apply the result obtained by purely electrical methods, that the ions travel about 1.6 cm. per second in a field of 1 volt per cm. The nuclei causing the rain-like condensation without exposure to Röntgen or radium rays are also removed by the action of an electric field; we have thus the direct proof that they also are ions. Recent experiments have proved that a charged conductor suspended within a closed space loses its charge by leakage through the air, and that the conduction shows all the peculiarities of that met with in an ionised gas. And, indeed, it appears that this ionisation is due to the action of radiation of the radium type from the walls of the vessel and from outside the vessel. The condensation method of detecting ions is, it may be pointed out, a very delicate one; a single ion if present in the vessel will be detected.

The positive and negative ions are not alike in their power of acting as condensation nuclei. In most of the experiments shown to-night the negative ions alone have in fact come into action. The positive require a considerably greater expansion in order that water may condense upon them. The final volume must for the positive ions be about 1.31 times the initial instead of only 1.25, corresponding to a six-fold instead of a four-fold supersaturation.

To demonstrate the difference between the positive and negative ions the same form of apparatus is used as in the previous experiment. Instead, however, of a difference of potential of 200 volts, only two or three volts are applied between the plates. And in this experiment only a thin layer close to the lower plate is exposed to the action of the rays. Under these conditions, if the upper plate is the positive one, the negative ions will be attracted upwards out of the ionised layer, and will occupy the greater part of the volume of the vessel, while the positive ones will have only a short distance to travel before reaching the lower plate. If the rays be cut off before the expansion is made it is easy to arrange the interval to be of such a duration that all the positive ions have been removed, while only a small fraction of the negative ions have reached the upper plate before the expansion takes place. Thus we can try the effect of expansion when the vessel is charged with practically negative ions only. By reversing the electrical field the action of positive ions, almost free from negative ions, can be studied. When the expansion

is between 1.25 and 1.31 a fog or a mere shower is obtained, according as the direction of the field is such as to drive negative or positive ions upward.

The ions are by no means the only nuclei which can be produced within moist air from which the dust particles have been removed. Among the most interesting of such apparently uncharged nuclei are those produced in moist air exposed to ultra-violet light. It is impossible in the time available to do more than allude to them here.

[C. T. R. W.]



Friday, March 11, 1904.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.  
President, in the Chair.

PROFESSOR FREDERICK T. TROUTON, M.A. D.Sc. F.R.S. M.R.I.

*The Motion of Viscous Substances.*

VISCOSITY is one of the more familiar phenomena. An excellent example of the behaviour of a viscous substance can be afforded by treacle or honey. For instance, on helping oneself to honey, the slow and leisurely way in which the substance leaves the spoon is only too patent. This is in marked contrast to liquids such as water which flow freely.

If we stir such a liquid as treacle, we experience a resistance, a force opposing the movement; on diluting the treacle with water less resistance is afforded by it to stirring—the liquid does not feel so thick.

Liquids of any desired thickness or viscosity intermediate between treacle and water may be prepared by mixing them in the proper proportions.

Another convenient series of substances can be easily made, beginning with benzine, which is a particularly mobile liquid, and ending with pitch, ordinarily viewed as a solid.

The substance next to benzine is just a little less easily stirred than it. Next to this we have a material a little thicker, and so on by slight increases until we arrive at pitch.

In considering this set of substances we see the difficulty there is in defining exactly what a liquid is. The members of the series, at one end, would be said by all to be liquid, while at the other end they appear at first sight equally entitled to be considered solid; but if we examine them carefully we find that as we go up the series each one can flow just like its neighbour only not quite so fast. Even the seemingly solid pitch flows when given time.

The question naturally suggests itself, How much is each one thicker or more viscous than the one next it in the series? This at once leads us to the further question, What is the precise meaning we propose to attach to the term viscosity?

Comparative measurements might be made of the rate at which the substances flowed under similar circumstances, and these made the basis of a scale of viscosity, but a clearer and more precise definition is got by having recourse to the more mechanical ideas used in the well-known definition of viscosity.

A good idea of the lines on which this is done may be obtained in this way. Imagine a cube of the viscous material standing on a

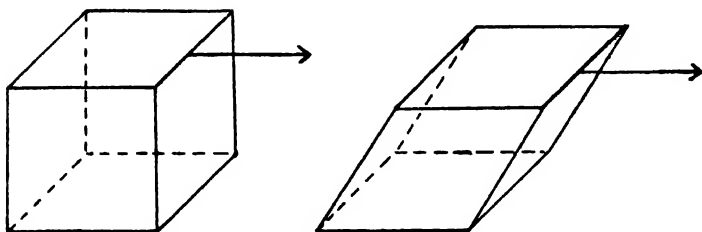
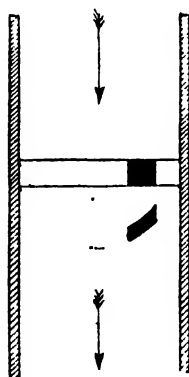


FIG. 1.

table (Fig. 1) to be gradually twisted over to the right by a force applied along the top. Then the slower the block twists the more viscous it is said to be.

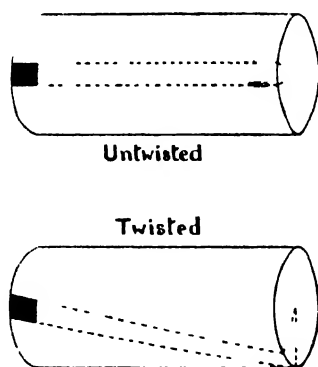
#### *Tube Method.*

The viscosity of the substances at the more liquid end of the benzine-pitch series, can be determined by observing the rate at which they can be forced to move through tubes under recognised conditions. Fig. 2 shows how a layer in such a tube lying between two cross



—FLOW IN TUBE—  
"  $\frac{F}{L} B$

FIG. 2.



$$\mu = \frac{2 T l}{\pi \omega R^4}$$

FIG. 3.

sections at any moment, becomes bent forward at its centre as the flow proceeds. The little square shown in the first position has taken up a skewed shape in the second. This helps us to see that we have in

this case the same kind of motion as contemplated in the definition above referred to. The subjoined table exhibits the determinations made in this way for five of the substances in the series.

### *Torsion Method.*

The viscosity in the case of the more viscous materials of the series was in the first instance determined by a method in which a column or rod was twisted round and round, one end being held. From the amount of the twist required to force it to turn at a given rate, the viscosity can be calculated. The table shows the value found in this way for several substances.

The apparatus employed in these determinations consisted in a horizontal shaft turning on anti-friction wheels, round which a cord

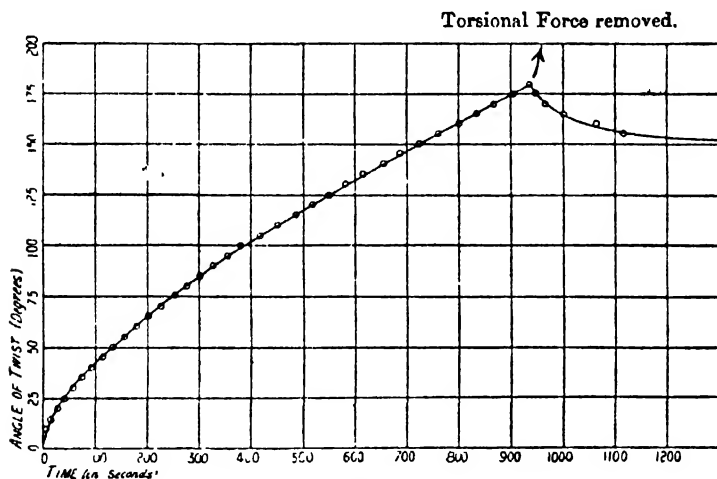


FIG. 4.

carrying a weight is wound. The weight unwinding the cord turns the shaft. A rod of the material to be tested is fixed in line between the end of the shaft and a stationary clamp. The rate at which the shaft turns is measured from a divided dial face. A knowledge of this and of the weight enables the viscosity to be calculated.

Fig. 3 will help us to understand that there is a direct connection between the simple alteration in shape dealt with in the definition of viscosity and the effect produced on the substance of the rod when twisting. The small square is seen in the second figure to have become bent in consequence of the twist imparted to the rod.

The results obtained with this apparatus are shown in Fig. 4. The curve shows the angle through which the rod had twisted at any moment after the application of the force.

"It will be seen that just at first it turns more rapidly than afterwards when it settles down to a uniform rate of twisting. It is apparently possible to keep on turning the rod as long as one pleases. By painting a white line down a rod, and then twisting it, a beautiful spiral line is produced. On removing the twisting force the rod turns back a short distance, at first rapidly, but slows down gradually to rest.

### *Traction Method.*

A very interesting question arises as to how the material moves in a rod of pitch or such-like substance when drawn out. If we subject a rod of pitch to traction, say by suspending it from one end and hanging weights from the other end, we find that it draws out at an approximate uniform rate. The rate is at first a little faster than it is later on; it however finally settles down to a uniform rate, provided the tension is kept the same. This is similar to the effect observed in the case of torsion. Also, as in the case of torsion, we get a slight recovery on removal of the force.

The exact way in which the particles move in a rod as it is drawn out is not at all clear. In the case of the flow through a tube, we know that the centre flows faster than the outer parts because the sides are held back. Nothing in the case of the rod corresponds to this. To try and observe the character of the flow in a rod the plan was tried of drawing out a rod made up of two shorter rods of different colours, but otherwise alike, joined end to end. The junction was made as sharp as possible and lay at right angles to the axis of the rod. Rods of shoemaker's wax and of glass were used. Difficulty was found in getting two differently coloured glasses of exactly the same fusibility, and also in forming a really sharp line of junction between them. As far as the observations go, they show at least that the particles lying in a plane do not move so as to lie on a curved surface, such as occurs in the flow through a tube.

Fig. 5 is intended to show how a small quantity of the material, included between two near planes, lies after a short time. A small cube of the material is shown in the initial stage and its subsequent shape when drawn out. The connection will thus be appreciated between the kind of movement here taking place, and that consistent with the definition of viscosity as illustrated by the model.

The rate of elongation of the rod divided by the tension gives us a coefficient of viscous traction. We have every reason to expect this to be about three times the viscosity of the material, and experiment supports this view. The value of the viscosity of pitch

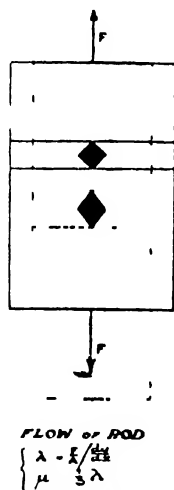
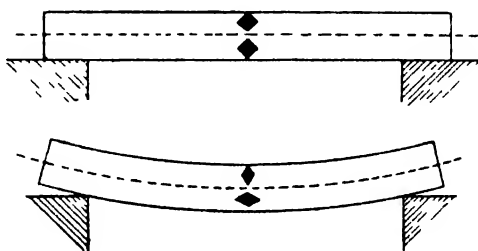


FIG 5

found in this way is shown in the table. The agreement with the values found by other methods is satisfactory for experiments of this character.

### *Bending of Bars.*

When a bar of pitch is laid horizontally, supported only at its ends, it sags in the middle. In doing so the upper parts of the



### SAGGING OF BEAM.

$$\lambda = \frac{5 \rho g L^3}{384 R D^3}$$

$$\mu = \frac{1}{3} \lambda$$

FIG. 6

material become compressed, while the lower are drawn out. This is shown in Fig. 6. Two little squares are put in to help us to under-

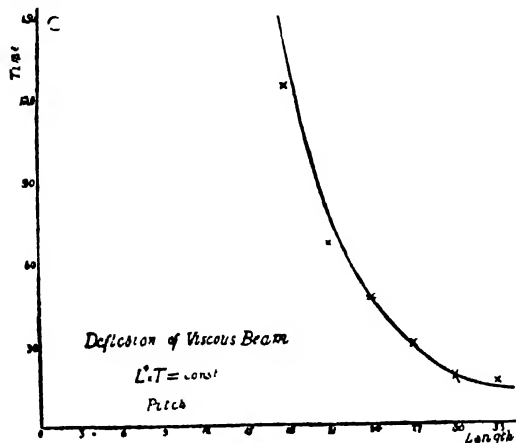


FIG. 7.

stand the movement of the material; these are subsequently transformed into the skew shape we have seen to be associated with viscous flow.

The upper square is compressed horizontally, the lower is drawn out in the same direction.

Experiment shows that the rate at which the bar falls at its centre is approximately that given by theory based on similar suppositions to those which were made in the case of traction.

Fig. 7 shows the time which, according to the theory, should be taken by rods of different lengths in falling at their centres through the same distance. The shorter the bar the slower it falls. The marked points are those actually observed. The agreement is, under the circumstances, satisfactory.

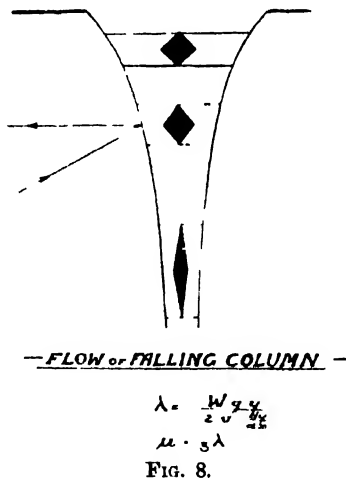
The results obtained in this way for the viscosity of several materials are exhibited in the tables. When the material of the bar is so soft that it sags too quickly to be easily observed, it may be immersed in a liquid of very nearly its own density. In this way the forces bending it can be made as small as we please and consequently the rate at which it sags also.

#### *Shape of Falling Stream.*

The shape of a falling stream of a viscous liquid is interesting to observe. It can be well seen when helping oneself to honey. If the liquid is a thick one we have practically a case of simple viscous traction of a rod continued until extreme thinning of the rod is produced. In Fig. 8 is shown the shape taken by such a liquid when falling from a circular hole in the bottom of the containing vessel.

There is an interesting point in connection with the shape or outline of the falling stream which is at first surprising. It comes out that, when the flow is slow, the same shape ought to be assumed by all substances under the same conditions as to size of orifice and height in containing vessel. This certainly appeared to be so in the case of the substances in the series examined. How this comes about will be understood by considering that if the material is removed slowly below owing to high viscosity, it is fed in at the top equally slowly.

A short length such as marked above draws out as it falls so that it occupies a greater length at subsequent positions. Now if we know the rate at which it is drawn out and the force acting upon it, we can calculate the viscosity just as in the direct experiments on traction.



In order to know the rate at which the material is being drawn out, two things are required. The amount of material passing down per second—this is easily found—and the slope of the surface to the vertical at the place in question. We can observe this on reflecting a beam of light from the surface of the column so as to pass out horizontally, by measuring the angle between the incident beam and the reflected one. So much for the rate of drawing out; now the

### VISCOSITY IN C G S UNITS

METHOD	SODA GLASS 575°	SODA GLASS 660°	SODA GLASS 710°	PITCH 104°	PITCH TAR $\frac{1}{8}$	PITCH TAR $\frac{3}{4}$	PITCH TAR $\frac{1}{2}$	TAR	TAR BENZ- $\frac{1}{2}$	BENZ-INE
TORSION	$11 \times 10^4$	$23 \times 10^{11}$	$45 \times 10^{10}$	$104 \times 10^9$						
TRACTION				$155 \times 10^{10}$						
BENDING BEAM				$109 \times 10^9$	$32 \times 10^7$	$26 \times 10^5$				
FALLING STREAM					$36 \times 10^7$	$37 \times 10^5$				
TUBE						$23 \times 10^6$	$83 \times 10^4$	520	24	007

other quantity required, the force of traction, is simply the weight of the suspended column situated below the point. By cutting off the column, collecting and weighing, we get its amount. It is true that the value of this varies slightly, for if a stream is watched it will be seen to grow longer and then break off when it gets too heavy to be supported, somewhere higher up. However, this goes on only at the end of the stream where it is extremely thin, and the alteration in weight thus produced may be safely neglected.

From the table it will be seen that the value of the viscosity so obtained is, on the whole, in satisfactory agreement with that obtained by other methods. It will be noticed that in the case of the thinner liquid, the inertia term which was neglected has probably made itself felt.

[F. T. T.]

Friday, March 25, 1904.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. F.R.S., Treasurer  
and Vice-President, in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*

*Liquid Hydrogen Calorimetry.*

IN the determination of quantities of heat, besides the "method of mixtures," the various calorimeters that have been used depend on liquefaction, evaporation, or condensation. One of the earliest, that of Laplace and Lavoisier—a development of Black's method—depended on the liquefaction of ice, care being taken to isolate the ice which was the calorimetric substance from any external heat effects, by means of a jacket of snow. In the middle of last century Bunsen devised an exceedingly delicate instrument in which ice was again the calorimetric substance; but instead of following Laplace and Lavoisier's plan of measuring the weight of ice melted, he took advantage of the reduction in volume of melted ice—namely, about one-eleventh part—to determine with great accuracy the quantity of heat that had been employed. As a unit of heat will melt  $\frac{8}{11}$  gramme of ice, this will produce a change of volume of about  $\frac{8}{11}$  cubic centimetre; and if the index tube of the instrument be half a millimetre in diameter, the unit of heat will be shown by about 6 or 7 millimetres on the scale. With such an instrument it is therefore possible to determine very accurately one-tenth of a gramme-calorie.

Professor Joly's calorimeter depends on condensation. In it the quantity of steam condensed on the body, which is the subject of experiment, is ascertained by weighing the amount of water formed. The body is contained in a chamber of relatively large volume into which the steam is suddenly admitted. It will be noticed, therefore, that the uncondensed steam in the chamber acts as a jacket to the body and prevents the passage of heat between it and external bodies; in this manner it is isolated from disturbing causes. In Professor Joly's hands, this instrument has been used to determine directly the specific heat of gases at constant volume.

Other methods have been adopted for the measurement of quantities of heat. Black compared the quantities of heat in two bodies of equal masses and temperatures, by noting the times in which they cooled to the same temperature. Regnault and others have used the



method of mixture, in which a given quantity of the substance to be experimented on at a higher temperature, is mixed with a given quantity of a known fluid substance at a lower temperature; from the final temperature acquired by the two, the quantity of heat given up by the former can be determined. In this method the main difficulty is the isolation of the mixture from external heating or cooling influences during the experiment, and its success in the hands of Regnault was due to the skill with which he accomplished this.

Evaporation is a means of absorbing heat; no evaporation can take place without absorption of heat, and usually this absorption is relatively great. The well known experiment of the freezing of water by its own evaporation by the methods of Leslie and Wollaston are illustrative of the use of the latent heat of evaporation to produce lower temperatures. Further, by a law of Dalton, evaporation takes place most copiously into a space which is kept free from vapour of the same kind as that coming off.

It has long been known that by the passage of air through volatile liquids a considerable reduction of temperature may be effected depending on the particular substance selected, the isolation of the liquid from external heat, and the use of air at the low temperature reached in each case. The following table gives the general results of the temperatures recorded by different experimenters when ether, sulphurous acid, methyl chloride, ammonia, and ethylene, were employed.

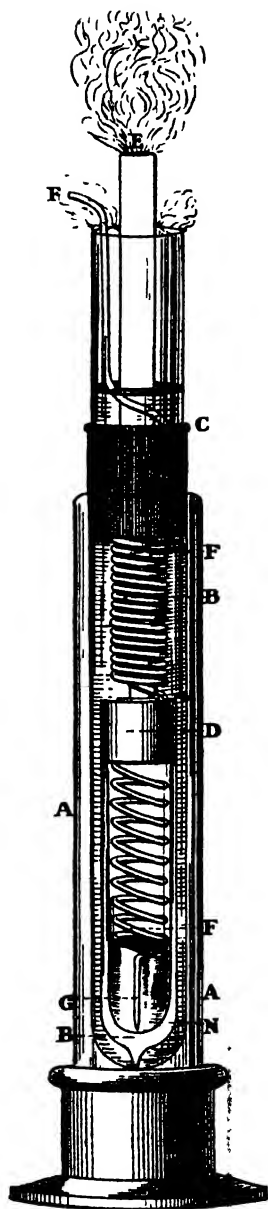
—	Temp C on Evaporation	Boiling Point	Critical Temperature.	Evaporation Temperature in terms of absolute Critical Temperature
Ether . . . .	- 34°	+ 35°	194°	.51
Sulphurous acid .	- 50°	- 10°	155°	.52
Methyl Chloride . .	- 55°	- 24°	141°	.53
Ammonia . . . .	- 87°	- 39°	130°	.46
Ethylene . . . .	- 132°	- 103°	10°	.50
Liquid Nitrogen with Hy- drogen passed through instead of Air as above .	- 214°	- 196°	- 146°	.47

It is interesting to notice that the limit of temperature reached by this means is in each case about half the absolute critical temperature. Thus for ethylene the absolute temperature of evaporation is 273° - 132°, or 141°, and its absolute critical temperature is 273° + 10°, or 283°, giving the ratio .50. Now if this approximate relation holds good for a substance like liquid nitrogen, then we should anticipate that by passing a current of a gas through it like

hydrogen, which at the temperature of boiling nitrogen is still a permanent gas, we should reach a temperature of  $-214^{\circ}$ ; and as this value would be just about the melting point, the nitrogen ought consequently to become solid.

The freezing of nitrogen by evaporation in a current of hydrogen at atmospheric pressure is carried out in the following way. Within a vacuum vessel A A, kept full of liquid air (Fig. 1), is inserted another vacuum vessel B B, which is held in its position by means of a cork C. About the middle of B B is fixed another cork D, which gives support to a tube E, allowing free passage between the lower part of B B and the atmosphere. F F F is a small tube coiled round the tube E as far down as the cork D, and below that continued as a coil in the lower part of B B, and ending in a nozzle at G. In the bottom of B B is placed a quantity of liquid nitrogen N. The experiment is conducted by passing pure hydrogen through the tube F, thereby cooling it to the boiling point of liquid air, and, finally, by means of the nozzle G through the liquid nitrogen. As the hydrogen passes down the spiral part of the tube F it is cooled to the temperature of the gaseous nitrogen rising from N, and bubbles through N at the temperature of the liquid nitrogen. These hydrogen bubbles are thus in the best condition, according to Dalton's law, to induce evaporation of the liquid nitrogen, without conveying unnecessary heat, and rapidly cause its temperature to fall. After a short time the hydrogen bubbles begin to move sluggishly in the cooling liquid nitrogen, and soon afterwards the nitrogen becomes solidified by its own evaporation. The appearance of the solid nitrogen as it is first formed is very extraordinary, as it deposits in long spiral tubes through which the hydrogen for a time escapes. As we now know that helium is as much more volatile a gas than hydrogen as the

FIG. 1.



latter is than nitrogen, we may safely predict that if a current of helium were similarly directed through liquid hydrogen, the latter would be reduced in temperature until it would freeze, seeing that the melting point of hydrogen is just about half its critical temperature.

An evaporation calorimeter, where the calorimetric substance is one of the liquefied gases, would be a convenient instrument provided it could be easily constructed and was reliable in its working. The efficiency of such an instrument depends (1) on the relatively large quantity of gas given by evaporation, and (2) on the great range of temperature easily available when liquid air, oxygen, nitrogen, or hydrogen is the calorimetric substance.

The following table gives the special physical constants of the various liquid gases that are of importance in calorimetry. That calorimetric substance will be the more sensitive which gives off

Liquid gases.	Boiling point.	Liquid volume 1 gramme at boiling point in c.c.	Latent heat in gramme-calories.	Volume of gas at 0° and 760 mm. per gramme-calorie in cubic centimetres.
Sulphurous acid	+ 10°·0	0·7	97·0	3·6
Carbonic acid .	- 78°·0	0·65 (solid)	142·4	3·6
Ethylene . .	- 103°·0	1·7 „	119·0	7·0
Oxygen . .	- 182°·5	0·9 „	53·0	13·2
Nitrogen . .	- 195°·6	1·3 „	50·0	15·9
Hydrogen . .	- 252°·5	14·3 „	125·0	88·9

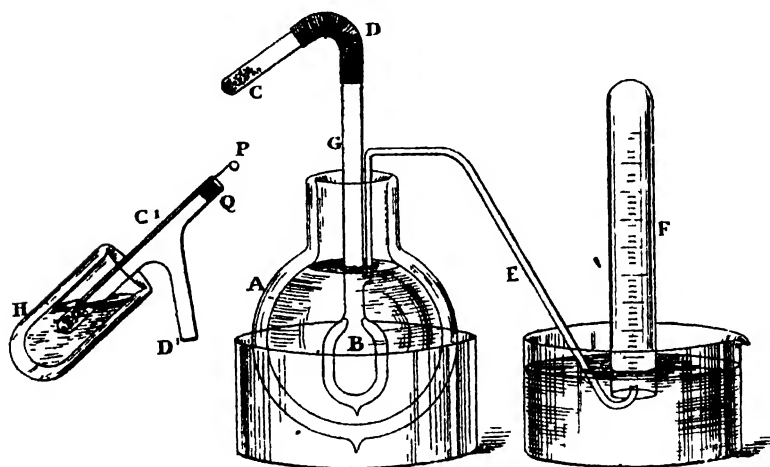
the larger volume of gas for a given quantity of heat. Thus oxygen gives 13·2 c.c. per calorie, while ethylene gives 7, hydrogen 88·9; hence oxygen is twice as sensitive as ethylene, and hydrogen six times as sensitive as oxygen. It is easy to detect a  $\frac{1}{10}$  gramme-calorie when liquid air is used, and as small a quantity as  $\frac{1}{360}$  can be observed with liquid hydrogen.

In selecting the calorimetric substance of a liquid gas calorimeter, hydrogen, as giving the greatest range of temperature and sensibility, would be the best; next to it would come nitrogen, then air, and lastly oxygen. But we must remember that we are enveloped in an atmosphere of air, and have to consider its effect. Passing over hydrogen for the present, let us examine the advantages and disadvantages of the other three gases. As the boiling point of air is below that of oxygen, even if there were no layer of cool oxygen gas on the surface of the liquid oxygen, the air coming in contact with it through the neck of the calorimeter would still remain gaseous. But if we were to take liquid nitrogen as the calorimetric substance, air, being heavier than nitrogen but having a higher boiling point, would, in falling down the neck of the calorimeter, come in contact with the

cool gaseous nitrogen and be condensed. Hence nitrogen would not be a convenient calorimetric substance. In any case, the boiling points of nitrogen, air, and oxygen being so close together, it is obvious that liquid air is the most convenient substance in the neighbourhood of  $-180^{\circ}$  to  $-200^{\circ}$  C.

The calorimeter has been described in my paper "On the Scientific Uses of Liquid Air,"\* and later an improved form in "Recherches sur les Substances Radio-Actives," by Madame Curie,† further a sketch of it is given in the paper on "The Absorption and Thermal Evolution of Gases occluded in Charcoal at Low Temperatures."‡ The annexed diagram shows its construction. It

FIG. 2.



consists essentially of a large vacuum vessel A, capable of holding two or three litres, into which is inserted the calorimeter, a smaller vacuum vessel B, of 25 to 50 c.c. capacity, which has been sealed on to a long narrow tube G, projecting above the mouth of A, and held in its place by some loosely packed cotton wool. From the side of this narrow tube, either before or after passing out of A, a branch tube, E, is taken off to enable the volatilised gas from the calorimeter to be collected in the receiver F, over water, oil, or other suitable liquid. To the extremity of the projecting tube G, a small test-tube C, to contain the portions of material experimented on, is attached by a piece of flexible rubber-tubing D, thus forming a movable joint,

\* Roy. Inst. Proc. 1894, vol. xiv., p. 398.

† 2nd Edition, p. 100.

‡ Roy. Soc. Proc. 1904, vol. lxxiv., p. 123.

which can be bent so as to tilt a few of the small pieces of substance contained in C into the calorimeter, and which afterwards assumes a position of rest somewhat like that in the diagram.

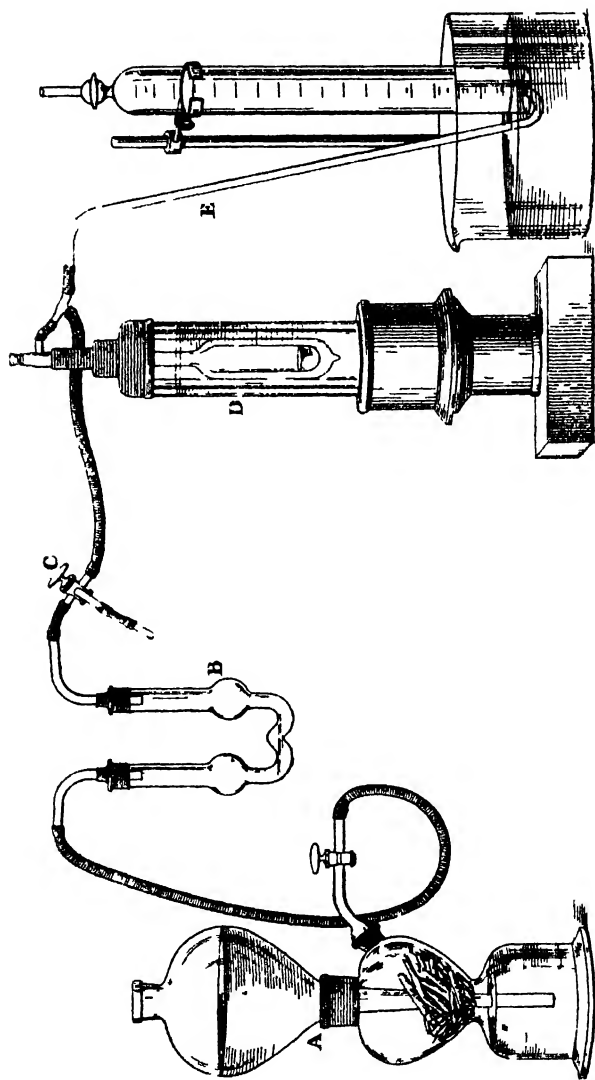
With care one can manage to tilt a single piece at a time from C' into B, but an improved form of this receptacle is shown at C' D'. In it, P is a wire movable through the cork Q, fitted into the mouth of the test-tube C', attached by a branch through the stiff rubber tube D' to the end of G, as before. At the end of the wire P is a hook, by which one piece of the substance at a time can be pulled up and dropped into B'. When no other arrangements are made, the portions of matter experimented on are at the temperature of the room; but when lower temperatures are required initially, a vacuum vessel H containing either solid carbonic acid, liquid ethylene, air, or other gas, can be placed so as to envelop the test-tube C or C'; or if higher temperatures are required, the surrounding vessel may be filled with the vapour of water or other liquids.

Much study and handling of the instrument have brought out the following matters as essential to high efficiency. I have already pointed out that in the neighbourhood of  $-180^{\circ}\text{C.}$  to  $-200^{\circ}\text{C.}$  liquid air is the preferable substance to use, while liquid hydrogen enables observations to be made as low as  $-250^{\circ}\text{C.}$  The value of the vacuum of the calorimeter itself is much enhanced by making it a mercury vacuum; and further by having, previous to use, a good mercury deposit over its surface. This is attained by putting some liquid air into the calorimeter B and leaving it to stand for some time. When a quantity of liquid air has been undergoing volatilisation for a time, as the nitrogen evaporates more quickly than the oxygen, the boiling point rises slightly. Two points require attention in consequence of this; first, the maintenance of a constant temperature of the liquid air during any one series of experiments; next, the prevention of a tendency for the calorimeter B to "suck back" some of the already volatilised gas. Hence the exterior vessel A should be filled with a large quantity—some two litres—of *old* liquid air, containing a high percentage of oxygen, and the calorimeter itself should be filled with some of the *same* fluid. This will maintain very closely the constant temperature required. When any "sucking back" seems to be taking place, the calorimeter should be emptied and filled anew from the larger flask A. The tube between the calorimeter and the gas receiver should be of the size of wide quill tubing, and its lower end should be so arranged below the surface of the liquid in the collecting vessel, as to give no resultant pressure. With such precautions, results may easily be obtained correct to within 2 per cent.

The instrument having been set up and filled with liquid air, according to the above directions and precautions, an experiment is conducted by tilting up the little test-tube, previously cooled or heated, thereby dropping into the calorimeter a portion of any sub-

stance previously weighed. The substance, if left under normal conditions, in this way falls from the temperature of the room to that

FIG. 8.



of liquid air. The heat given up by it to the liquid air volatilises some of it, which is carried off by the branch tube and measured in

the graduated receiver F. Immediately preceding or following this observation, a similar experiment is made with a small portion of a selected standard substance, namely, lead. The quantity of lead is so chosen as to produce about the same volume of gas in the receiver as that supplied by the portion of substance experimented on. By this means, the circumstances of the two observations are made as similar as possible, and thereby many sources of error are eliminated.

When the hydrogen calorimeter is to be used, the temperature being so much lower than in the liquid-air calorimeter, we have to keep the ordinary atmosphere from entering the mouth of the tube G by means of a current of hydrogen. This is attained in the manner shown in Fig. 3. An ordinary Kipp apparatus A supplies hydrogen which, after being dried in the U-tube B, is allowed to pass by the stop-cock C to the calorimeter D and tube E. The hydrogen passes continually through the apparatus until the moment of beginning an experiment, when the stopcock C is turned and the hydrogen cut off.

In Fig. 4 are shown various forms of calorimeters which were experimented with in determining the best form for the calorimeter bulb. The final form adopted was that shown in D, Fig. 4. Stray globules of the liquid hydrogen might splash up on dropping the substances to be experimented on into the calorimeter, and get carried over into the gas receiver, but this cause of error was found to be negligible, provided the calorimeter was large enough.

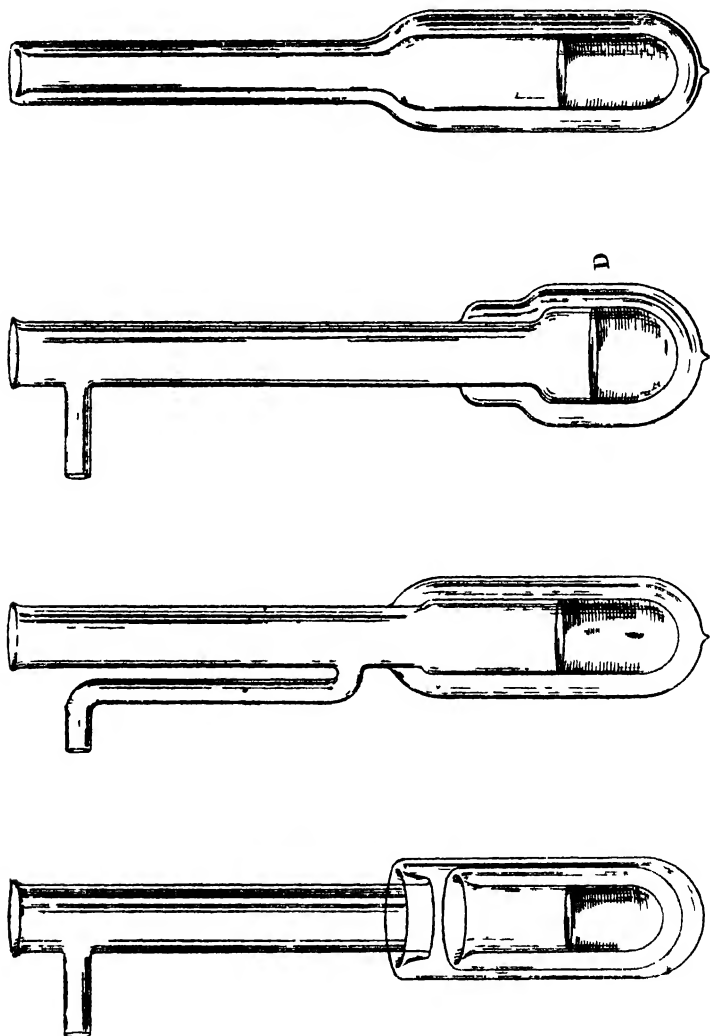
When the body has to be transferred from solid carbonic acid or liquid air to the calorimeter, the following procedure is adopted. It is placed in the small test tube, above the indiarubber joint, which is inserted into a small vacuum vessel containing some of the substance (solid carbonic acid or liquid air), so that at the moment of making the experiment the solid, by a quick vertical movement of the vacuum vessel, is thrown into the calorimeter. A little cotton wool inserted in the mouth of the vacuum vessel prevents the carbonic acid paste, or liquid air, from being ejected.

Observations were made to determine what allowance had to be made for loss of heat while the small body was falling down the tube B; also for similar losses by impacts on the sides of the indiarubber joint and of the glass tube. The substances used were lead, diamond, and graphite, and as the errors in any case did not exceed one-half to two-thirds per cent., they may in general be neglected.

The calorimeter may be put to various uses. Thus, on passing down the tube of the calorimeter wires of copper, iron, and german-silver, and noting the different rates at which the gas is evolved, we see that it is about six times more rapid with copper than with iron, and nine times more rapid than with german-silver, while with small rods of glass or ebonite no gas is produced in a short period of time. Again, we may measure the heat given up by condensation. Thus, if a small bulb containing some carbonic acid

be inserted into the calorimeter, immediately a rapid evolution of gas takes place, until at last the carbonic acid is frozen, and after a little time the evolution ceases. The volume of gas produced from

FIG. 4.



the same bulb exhausted is naturally very much less. But we may use the instrument for quite different purposes. Thus, in a small bulb is placed a mixture of hydrogen and oxygen in the proportions



in which they exist in water. Two insulated wires are let into the bulb, by means of which, on attaching them to an induction coil, we can explode the gases by the electric spark. The instant the explosion takes place, a corresponding vaporisation of liquid air follows, and from its amount as shown in the receiver we can determine the heat of combination of oxygen and hydrogen. In a similar manner the heat of the electric spark itself can be determined. Two fine wires, each passing through a fine glass tube, are passed down into the calorimeter until their ends are below the liquid surface, or they may be connected to a small sparking tube immersed in the liquid air. On attaching them to the induction coil and making contact, a spark passes in the liquid, or in the glass bulb, which immediately evaporates some of it, and from its gas volume in the receiver we find the heat generated by the spark.

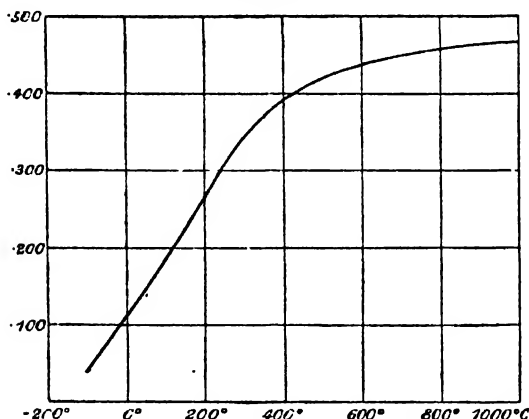
The determination of specific heats and latents is a matter of great importance. Latent heats of evaporation are usually determined under the ordinary atmospheric pressure: alteration of pressure has, in general, but a small effect on the latent heat of solidification. Specific heats, on the other hand, vary with the temperature, so that it becomes important to measure them at various temperatures. This is usually done by observing the mean specific heats over finite ranges of temperature, as, for example, between the boiling point of water and its freezing point, between the freezing point of water and the boiling point of carbonic acid, between this latter point and the boiling point of oxygen, and between this and the boiling point of hydrogen; or, we may go upwards, say, from the boiling point of water to the melting point of paraffin, then to the boiling point of sulphur, and so on. As so many properties of substances tend either to a maximum or a minimum, as we approach the absolute zero, there is great interest in examining the values of the specific heats of substances at low temperatures. Dulong and Petit discovered a simple, and very general law, according to which the product of the specific heat of a substance, in the solid state, and its atomic weight is constant. For example, let us take two small pieces of metal of equal weight— one, lead, with the high atomic weight of 207; the other, aluminium, whose atomic weight is only 27. On comparing the evolution of gas when the lead is put into the calorimeter, with that of the aluminium under the same circumstances, the very marked excess of the evaporation with aluminium over that with lead is at once apparent, and even a rough measure of the relative amounts of gas evolved shows one to be almost seven times that of the other, a ratio very nearly equal to that of their inverse atomic weights.

Two of the most interesting substances to study in this connection are carbon, in its two forms, diamond and graphite, and ice.

A large series of observations were made upon carbon in both its forms, the ranges of temperature being from about  $18^{\circ}$  C. to the boiling point of carbonic acid, thence to the boiling point of oxygen,

and finally to the boiling point of hydrogen. Early determinations of the specific heat of carbon in any of its forms had shown complete departure from the law of Dulong and Petit. In 1872 Professor H. F. Weber and myself,\* working independently, found that, as the temperature increased, the specific heat of carbon, whether as diamond or as graphite, continued to increase. Professor Weber found that "the specific heat of the diamond is tripled when the temperature is raised from  $0^{\circ}$  to  $200^{\circ}$ ," and my experiments showed that the mean specific heat of carbon from  $30^{\circ}$  to the boiling point of zinc was  $0.32$ , and to the temperature of the oxy-hydrogen blow-pipe (some  $2000^{\circ}\text{C}.$ ) it rose to  $0.42$ , and I added "the true specific heat at

FIG. 5.



$2000^{\circ}$  must be at least  $0.5$ ; so that at this temperature carbon would agree with the law of Dulong and Petit." In 1875† Professor Weber published the results of further experiments, proceeding by successive stages up to  $1000^{\circ}\text{C}.$ , and showing "that from the point (about  $600^{\circ}$ ) at which the specific heat of carbon ceases to vary with increase of temperature, and becomes comparable with that of other elements, any real difference in the specific heats of the two modifications disappears, and carbon obeys the law of Dulong and Petit."

Professor Weber plotted his results, taking specific heat as the ordinate, to temperature as the abscissa, and producing a curve like the old English *f*. He found the point of inflection for diamond

\* H. F. Weber, "The Specific Heat of Carbon," *Phil. Mag.* 1872, ser. 4, vol. xlv., p. 251. J. Dewar, "The Specific Heat of Carbon at High Temperatures," *l.c.*, p. 461.

† *Phil. Mag.* 1875, ser. 4, vol. xlix., p. 285.

about  $60^{\circ}\text{C}$ ., and for graphite about  $0^{\circ}\text{C}$ . But for this discovery, the trend of the curve, as shown in the diagram, Fig. 5, would have pointed to the vanishing of the specific heat of carbon about  $-90^{\circ}\text{C}$ ., a result which could not be accepted as final. The investigations carried out recently,\* have cleared up this point, and verified the existence of the points of inflection. The following table summarises my observations on the specific heats of diamond, graphite, and ice :—

Substance	$18^{\circ}$ to $-78^{\circ}\text{C}$ ., or, at $-30^{\circ}\text{C}$ .	$-78^{\circ}$ to $-188^{\circ}\text{C}$ , or, at $-133^{\circ}\text{C}$ .	$-188^{\circ}$ to $-252^{\circ}\text{C}$ , or, at $-220^{\circ}\text{C}$ .
Diamond . . . .	0.0794	0.0190	0.0043
Graphite . . . .	0.1341	0.0599	0.0138
Ice . . . . .	0.463*	0.285	0.146

\* This is from  $-18^{\circ}$  to  $-78^{\circ}$  in the ice experiment.

These results for diamond and graphite accord well with those of Professor Weber over common ground. He gives 0.0806 for the diamond between  $21\frac{1}{2}^{\circ}$  and  $-80^{\circ}$ , and 0.1301 for graphite over the same range.

The second curve in the diagram, Fig. 6, shows the sequence between Professor Weber's results and my continuation to low temperatures, and demonstrates the reversal of the curvature of the curve at low temperatures. Similar results were got for carbon.

The results for ice follow much the same order of change. A reference to the table above shows that the mean specific heat of ice falls from 0.463 at  $-46^{\circ}$ , to 0.285 at  $-133^{\circ}$ , and 0.146 at  $-220^{\circ}\text{C}$ .; that is, in the lowest range of temperature between the boiling points of oxygen and hydrogen, it is only one-third of its value between  $-18^{\circ}$  and the temperature of boiling carbonic acid.

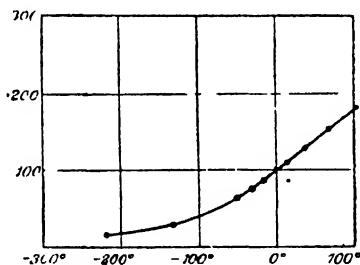
It would be a matter of interest to investigate the general behaviour of various groups of substances, as regards their specific heats at low temperatures. Without having attempted any careful systematic investigation, the following observations extracted from laboratory records are fairly representative of some classes of bodies. In the table the specific heats of two alloys are given, which were used in the course of the investigation; also those of sulphur, selenium, and tellurium. Two alums, on which Kopp had made some observations, were included in the research, together with three other typical salts. Again, naphthaline and paraffin were a pair, whose specific heats were examined; also the chloride, bromide, and iodide of silver. The results for the solidified gases, carbonic acid, ammonia, sulphurous acid, were of obvious interest,

No. of obs.	Substance.	Weight used in grammes.	Range of Temperature. Degrees Centigrade.	Vol. of Gas in cubic centimetres	Specific Heat.
1	German silver . . .	0.22	- 18 to -188	48	0.080
1	Brass . . . . .	0.627	+ 19.5 -188	166	0.099
1	" . . . . .	0.244	-188 -252.5	66 (H)	0.048
2	Tellurium . . . . .	0.645	+ 18.2 -188	99.5	0.047
2	Sulphur . . . . .	0.289	+ 18.2 -188	131	0.137
2	Selenium . . . . .	0.353	+ 18.2 -188	80	0.068
2	Potassium alum . . .	0.180	+ 18.8 -188	152.5	0.256
2	" " . . . . .	0.376	- 78 -188	180	0.223
2	Chromium alum . . .	0.20	+ 20 -188	162	0.243
2	" " . . . . .	0.392	- 78 -188	135	0.222
1	Calcium chloride (hydrate)	0.184	+ 20 -188	180	0.294
1	" " "	0.336	- 78 -188	141	0.271
3	Sodium chloride . . .	0.105	+ 16 -188	55.2	0.187
2	" " . . . . .	0.253	- 78 -188	65.5	0.164
3	Ammonium chloride . .	0.054	+ 16 -188	45.8	0.300
2	" " . . . . .	0.130	- 78 -188	42.5	0.207
2	Naphthaline . . . . .	0.55	+ 16 -188	31.5	0.202
2	" . . . . .	0.105	+ 16 -188	57.25	0.194
1	" . . . . .	0.090	+ 15 -188	50.5	0.204
2	" . . . . .	0.203	- 78 -188	40.6	0.126
1	Paraffin . . . . .	0.08	+ 15 -188	68.5	0.312
1	" . . . . .	0.105	- 78 -188	38.5	0.176
1	Silver iodide . . . . .	0.307	+ 16 -188	44.5	0.052
2	" bromide . . . . .	0.196	+ 16 -188	35.5	0.064
2	" chloride . . . . .	0.215	+ 16 -188	49.75	0.082
5	Solid carbonic acid . .	0.164	- 78 -188	57.1	0.215
1	" " " . . . . .	0.15	- 78 -182.5	50	0.225
1	" " " . . . . .	0.190	- 78 -182.5	62	0.223
2	Solid ammonia . . . .	0.14	-103 -188	72.25	0.519
2	" " . . . . .	0.156	-103 -188	77.5	0.490
3	Solid sulphurous acid .	0.325	-103 -188	75.2	0.223
3	" " . . . . .	0.311	-103 -182.5	57.3	0.236
2	Ceylon thoria mineral .	0.500	+ 15 -188	70.6	0.044

and several observations on them are given. With regard to these bodies, it may be noted that the values found are not far removed from those of the specific heats at constant volume in the gaseous state, and I have no doubt that if the experiments had been extended to temperatures between that of liquid air and hydrogen these results would all have been below the gas constant. The other bodies examined all show diminution of specific heat at the lower temperatures, the most marked examples being the hydrocarbons, paraffin and naphthaline.

While the experiments on the specific heats of diamond graphite and ice were being carried on, the frequent determination of the quantities of gas evaporated by lead in the same circumstances as the diamond graphite or ice under investigation, afforded means for the direct measurement of the latent heats of evaporation of hydrogen, nitrogen, air, and oxygen. Lead had been selected as the metal of comparison for the following reasons:—its low specific heat enabled

FIG. 6.



small quantities of heat to be conveyed into the calorimeter while the mass of the metal was still considerable; further, the variations of the specific heat of lead with temperature are small, and its specific heat may hence be treated as a linear function of the temperature; and lastly, the metal is easily obtained very pure.

In this manner the latent heat of hydrogen, whether determined by dropping small pieces of lead through a range of temperature as great as  $270^{\circ}$ , or through as short a range as  $64^{\circ}$ , was found to be about 121 to 122 gramme-calories. In my Bakerian Lecture,\* having assumed what at the time appeared to be the value of the latent heat of hydrogen, namely, 200 gramme-calories, and having observed experimentally that 15 per cent. of the liquid had to be quickly evaporated under exhaustion to reduce the temperature to the melting point of hydrogen, I deduced the mean specific heat of the liquid between the boiling point and the freezing point to be about 6. The present investigation enables me to correct this statement, the value

\* Proc. Roy. Soc., June 1901, vol. lxxvii. p. 361.

of the mean specific heat in question being in reality about 3.4 instead of 6. This correction removes hydrogen from the list of substances which follow Dulong and Petit's law, its atomic heat being only about half the required amount. In an early communication to the Royal Society of Edinburgh,\* I showed that the specific heat of hydrogen absorbed by palladium was about 3.5. It seems therefore that hydrogen in the gaseous, the occluded, and the liquid condition, has substantially the same specific heat.

It is of interest to see what support can be got for the value of the latent heat of hydrogen being about 121 or 122. From some early observations of mine with the helium thermometer on the vapour pressure of hydrogen below the boiling point, a Rankine formula was obtained,

$$\log p = 5.5038 - \frac{53.13}{t}$$

which, combined with Clapeyron's equation, where account was taken of the difference of the specific volumes of hydrogen in the liquid and the gaseous states at the boiling point, gave 120.3 as the latent heat of liquid hydrogen. Similar treatment of Travers'† smoothed results gave 119. Two Willard Gibbs' formulæ calculated from results evenly selected from these actual observations gave 123.4 and 117.5, or a mean of 120.5.

For nitrogen, the value of the latent heat was found to be about 50.4 gramme-calories at the boiling point. Other observers (Fischer and Alt, Alt, Shearer) give the values of this quantity as 48.9, 48.7 (at 718 mm. pressure), 52.07 (at 96 mm. pressure), and 49.8. The application of a Rankine formula deduced from my own observations,

$$\log p = 6.6462 - \frac{292}{t},$$

gave 48.0; while the same process applied to observations of Fischer and Alt gave 49.65, and a Willard Gibbs' formula gave 51.4.

In the case of oxygen its latent heat was found to be 51.15 gramme-calories. Several experimenters have found the value of this quantity to be as high as 58.0, 60.9, 61.0. A careful direct determination of Alt's gives 52.07 (725 mm.) and 58.85 (68 mm.). By means of Rankine and Willard Gibbs' formulæ, calculated from the observations of Olzewski, Estreicher, and Travers, I have found the values 51.4, 52.53, 53.78.

These indirect methods of determining the latent heat depend on formulæ of which only the principal terms are retained. We cannot, therefore, expect more than approximate values from them, so that it is sufficient at present to show that the direct experimental values found in the above series of observations substantially agree with those obtained by indirect and approximate calculations.

\* "The Physical Constants of Hydrogenium," Trans. Roy. Soc. Ed. 1873.

† Phil. Trans., 1902, A., vol. cc. p. 169.

In passing, it may be noticed that if the constancy of Trouton's constant is to be accepted, the latent heat of oxygen should be greater than that of nitrogen—a result in accordance with the above values.

The latent heat of air will depend on its constitution, tending towards equality with that of oxygen in the case of *old* liquid air, which is rich in oxygen. In an early experiment, I found the latent heat of air to be 49·7 gramme-calories; in a later one, it was 58·41. I then made a series of experiments in which a succession of half-grammes of lead, 10 or 12 at a time, were dropped into old liquid air; from these 53·63 gramme-calories were found. These values approach those of Fenner and Richtmyer's,\* found by an electrical method.

During the time Professor Curie lectured at the Royal Institution, some measures of a preliminary kind were jointly made by us of the rate at which radium bromide gives out energy at low temperatures. The quantity of radium bromide was 0·42 grm.; and it was used both in a liquid oxygen and liquid hydrogen calorimeter. The thermal evolutions are given below :

		Gas Evolved per minute.	Calories per hour.	
Liquid oxygen	.	5·5 c.c.	22·8	} Crystals.
Liquid hydrogen	.	51·0 "	31·6	
Melting ice	.	—	24·1	
Liquid oxygen	.	2·0 "	8·3	After fusion.
Liquid oxygen	.	2·5 "	10·3	Emanation condensed.

The apparent increase of heat evolution at the temperature of liquid hydrogen was probably due to the calorimeter being too small, so that hydrogen spray was carried away with the gas, thus making the gas volume too great, and inferentially the heat evolved.

I have to acknowledge the valuable aid I have received from my Chief Assistant, Mr. Robert Lennox, F.C.S., and that of his colleague, Mr. J. W. Heath, F.C.S.

[J. D.]

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\* Phys. Rev., 1905, vol. xx. p. 81.

Friday, June 3, 1904.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR SVANTE ARRHENIUS, of Stockholm, *Hon. Mem. R.I.*

*The Development of the Theory of Electrolytic Dissociation.*

At first sight nothing seems to be more evident than that everything has a beginning and an end, and that it is possible to divide everything. Nevertheless, the philosophers of antiquity, especially the Stoicists, concluded on purely speculative grounds, that these opinions are not at all necessary. The wonderful development of science has reached the same conclusion as these philosophers, especially Empedocles and Democritus, who lived about 500 years B.C., and for whom the ancients had already a vivid admiration.

Empedocles professed that nothing is made of nothing, and that it is impossible to annihilate anything. All that happens in the world depends upon a change of form, and upon the mixture or the separation of bodies. Fire, air, water and earth are the four elements of which everything is composed. An everlasting circulation is characteristic of Nature.

The doctrine of Democritus still more nearly coincided with our modern views. In his opinion bodies are built up of indefinitely small indivisible particles, which he called atoms. These are distinguished by their form and magnitude, and also give different products by their different modes of aggregation.

This atomic theory was revived by Gassendi about 1650, and then accepted by Boyle and Newton. The theory received a greatly increased importance by the discovery by Dalton of the law of multiple proportions. For instance, the different combinations of nitrogen with oxygen contain, for each unit weight of nitrogen, 0.57, 1.14, 1.72, 2.29 or 2.86 unit weights of oxygen.\* Between these combinations there is no intermediate proportion. This peculiarity is characteristic of chemistry in contradistinction to physics, where the more simple continuous and gradual transition from one state to another prevails. This difference between the two sister-sciences has often caused controversies in the domain of physical chemistry. The occurrence of discontinuous changes and of

\* To explain this we suppose, in accordance with Dalton, that the molecules of the different combinations of nitrogen with oxygen contain two atoms of nitrogen and one, two, three, four or five atoms of oxygen.



multiple proportions has frequently been assumed, when a closer investigation has found nothing of the sort.

The law of multiple proportions is the one fundamental conception upon which modern chemistry is built up. Another is the law of Avogadro, which asserts that equal volumes of different gases under like conditions of temperature and pressure contain the same number of molecules. This conception, dating from the beginning of the nineteenth century, was at first strongly combated, and it was its great value in explaining the new discoveries in the rapidly growing domain of organic chemistry which led to its general acceptance in the middle of the past century, after Cannizzaro had argued strongly in its favour.

There were, however, some difficulties to be removed before Avogadro's law could be accepted. For instance, it was found that the molecular volume of sal-ammoniac,  $\text{NH}_4\text{Cl}$ , in the gaseous state was greater than might be expected from its chemical composition. This led to the supposition that the molecules of sal-ammoniac when in the gaseous state are partially decomposed into ammonia,  $\text{NH}_3$ , and hydrochloric acid,  $\text{HCl}$ . Indeed v. Pebal and v. Than succeeded in showing that this really happens. They used an apparatus that is shown in the annexed figure (Fig. 1). Two coaxial tubes are placed the one inside the other by means of a cork. The outer tube was closed at its upper end, the inner one was open, and contained at C a diaphragm of asbestos and above that a piece of sal-ammoniac. The upper end was heated by an air-bath, so that the piece of sal-ammoniac was volatilised. After this a current of hydrogen was led through both glass-tubes D and E. Now ammonia diffuses more rapidly than hydrochloric acid; if, therefore, the vapour of sal-ammoniac is partially decomposed into ammonia and hydrochloric acid, we should expect that above the asbestos diaphragm there would be an excess of hydrochloric acid and beneath it an excess of ammonia. This v. Pebal showed to be the case. The hydrogen-current from D showed an acid reaction on a piece of litmus-paper in A, and that from E showed an alkaline reaction on a similar piece of litmus-paper placed in B. It was objected that the decomposition might

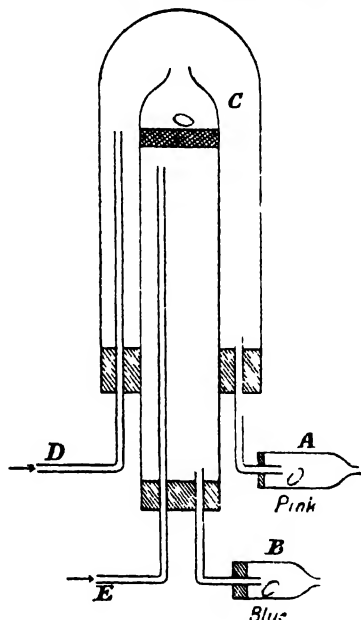


FIG. 1.

possibly be caused by the asbestos of the diaphragm, or by the hydrogen. v. Than, therefore, made a diaphragm of sal-ammoniac, and substituted nitrogen for hydrogen, but the effect was the same.

These experiments were performed in the years 1862 and 1864. They were based on the doctrine of dissociation, which was at that time (1857) worked out by Ste. Claire-Deville, and developed by his pupils. From the most ancient times use was made of the fact that limestone at high temperatures gives off carbonic acid, and that quicklime remains. This and similar processes were studied by Ste. Claire-Deville. He found that the same law is valid for the pressure of carbonic acid over limestone and for the pressure of water vapour over liquid water at different temperatures. On these fundamental researches the theory of dissociation was based, a theory which has subsequently played an ever-increasing rôle in chemistry, and whereby a broad bridge was laid between physical and chemical doctrines.

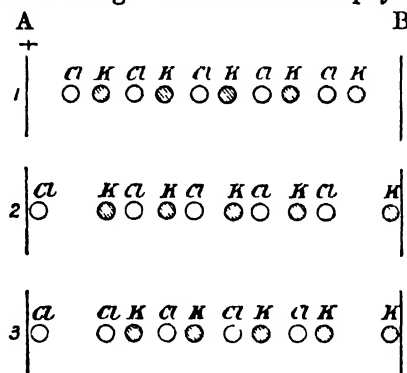


FIG. 2.

At almost exactly the same time we find in the writings of Clausius on the conductivity of salt solutions the first traces of an idea that salts or other electrolytes may be partially dissociated in aqueous solutions. Buff had found that even the most minute electric force is sufficient to drive a current through a solution of a salt. Now after the scheme of Grotthuss, at that time generally accepted, the passage of the electric current through a solution is brought about in such manner that the conducting molecules, e.g. of potassium chloride (KCl), are divided into their ions, which combine again with one another in the following manner. At first, as the current is closed, the electrode A becomes positive and the electrode B negative. All the conducting molecules KCl arrange themselves so that they turn their positive ions (K) to the negative electrode B, and their negative ions (Cl) to the positive electrode A. After this, one chlorine ion is given up at A and one potassium ion at B, and the other ions recombine, so that the K of the first molecule takes the Cl of the second molecule, and so on (Fig. 2). Then the mole-

cules turn round under the influence of the electric force, so that we get the scheme 3 and a new decomposition can take place. This represents the Grotthuss' scheme, that supposes continuous decompositions and recombinations of the salt molecules.

As such exchanges of ions between the molecules take place even under the influence of the weakest electromotive forces, Clausius concluded that they must also take place if there is no electric force, i.e. no current at all. In favour of his hypothesis he pointed to the fact that Williamson, as far back as 1852, in his epoch-making theory of the formation of ethers, assumed an analogous exchange of the constituents of the molecules. At this exchange of ions it might sometimes, though extremely rarely, happen that an ion becomes free in the solution for a short time; at least such a conception would be

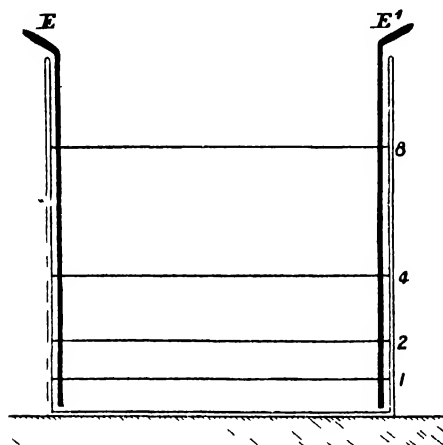


FIG. 3.

in good agreement with the mechanical theory of heat, as it was developed by Kronig, Maxwell, Clausius and others at that time.

In the meantime, Bouty, and particularly Kohlrausch worked out the methods of determining the electric conductivity of salt solutions. In 1884 I published a memoir on this subject. I had found that if one dilutes a solution—e.g. of zinc sulphate—its conductivity per molecule, or what is called its molecular conductivity, increases not infinitely, but only to a certain limit. We may figure to ourselves an experiment performed in the following manner (Fig. 3). In a trough with parallel walls there are placed close to two opposite sides two plates of amalgamated zinc,  $E E_1$ . On the horizontal bottom of the vessel there is placed a layer of solution of zinc-sulphate that reaches the level 1. The conductivity may be  $k_1$ . After this has been measured we pour in so much water, that after stirring the solution the level reaches 2, which lies as much above 1 as this lies above the bottom.

The conductivity is then found to be increased, and to have the value  $k_2$ . Increasing in the same manner, the volume, by addition of pure water until it is doubled, the level 4 is reached, and the conductivity is found to be greater than in the previous case—say  $k_4$ . So we may proceed further and further; the conductivity increases, but at the end more slowly than at the beginning. We approach to a final value,  $k_\infty$ . This is best seen in the next diagrams, which represent the newer determinations of Kohlrausch (Figs. 4, 5).

I explained this experiment in the following manner. The conductivity depends upon the velocity with which the ions (Zn and  $\text{SO}_4$ ) of the molecules ( $\text{ZnSO}_4$ ) are carried through the liquid by

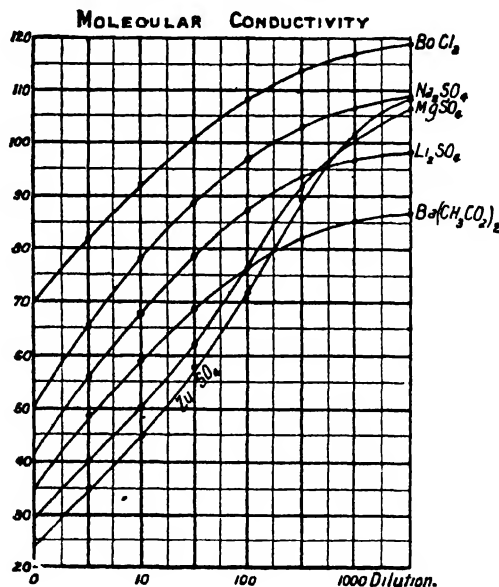


FIG. 4

the electric force, i.e. the potential difference between  $E$  and  $E_1$ . If this potential difference remains constant, the velocity depends only on the friction that the ions in their passage through the liquid exert on the surrounding molecules. As these, at higher dilutions, are only water molecules, it might be expected that the conductivity would remain constant and independent of the dilution if it be supposed that all molecules,  $\text{ZnSO}_4$ , take part in the electric transport. As experiment now teaches us that the molecular conductivity increases with the dilution, even if this is very high (1000 or more molecules of water to one molecule of  $\text{ZnSO}_4$ ), we are led to the hypothesis that not all, but only a part of, the  $\text{ZnSO}_4$  molecules

take part in the transport of electricity. This part increases with the dilution in the same proportion as the molecular conductivity  $k$ . The limiting value  $k_s$  is approached at infinite dilution, and corresponds to the limit that all molecules conduct electricity. The conducting part of the molecules I called the active part. It may evidently be calculated as the quotient  $k : k_s$ .

If now this new conception were only applicable to the explanation of the phenomena of electric conductivity, its value had not been so very great. But an inspection of the numbers of Kohlrausch and others for the conductivity of the acids and bases, compared with the measurements of Berthelot and Thomsen on their relative strength

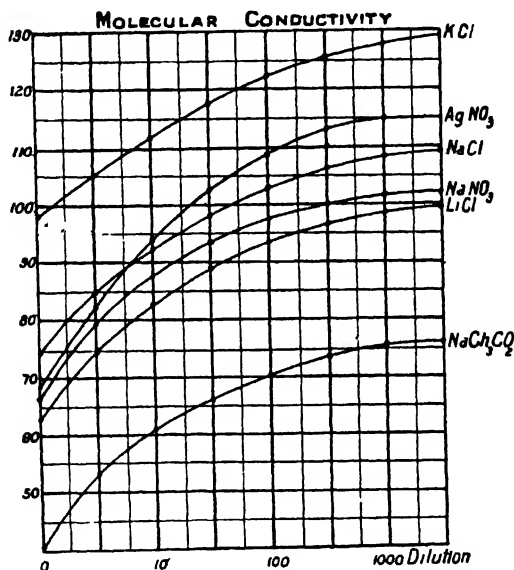


FIG. 5

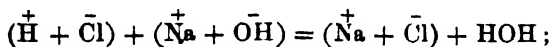
with regard to their chemical effect, showed me that the best conducting acids and bases are also the strongest. I was thereby led to suppose that the electrically active molecules are also chemically active. On the other hand the electrically inactive molecules are also chemically inactive. In this connection I would mention the remarkable experiments of Gore, which were easily explained by the new manner of view. Concentrated hydrochloric acid, free from water, has no action on oxides or carbonates. Now this hydrochloric acid is almost incapable of conducting the electric current, whereas its aqueous solutions conduct very well. The pure hydrochloric acid contains, therefore, no (or extremely few) active molecules, and

this agrees very well with the experiments of Gore. In the same way we explain the fact that concentrated sulphuric acid may be preserved in vessels of iron plates without destroying them, whereas this is impossible with the diluted acid.

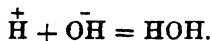
An unexpected conclusion may be deduced from this idea. As all electrolytes in extreme dilution are completely active, then the weak acids must increase in strength with the dilution, and approach to the strength of the strongest acids. This was soon afterwards shown by Ostwald to agree with experiments.

The Norwegian natural philosophers, Guldberg and Waage, had developed a theory according to which the strength of different acids might be measured as well by their power of displacing another acid in solutions as by their faculty to increase the velocity of chemical reactions. Therefore, we may conclude that the velocity of reaction, induced by an acid, would be proportional to the quantity of active molecules in it. I had only a few experiments by Berthelot to demonstrate this proposition, but in 1884, Ostwald published a great number of observations that showed this conclusion to be true.

The most far reaching conclusion of the conception of active molecules was the explanation of the heat of neutralisation. As this is much more easily understood by means of the theory of electrolytic dissociation, I anticipate this for a moment. According to this theory strong acids and bases, as well as salts, are at great dilution (nearly) completely dissociated in their ions, e.g.  $\text{HCl}$  in  $\text{H}^+ + \text{Cl}^-$ ,  $\text{NaOH}$  in  $\text{Na}^+ + \text{OH}^-$  and  $\text{NaCl}$  in  $\text{Na}^+ + \text{Cl}^-$ . But water is (nearly) not dissociated at all. Therefore the reaction of neutralisation at mixing a strong acid, e.g.  $\text{HCl}$  with a strong base, e.g.  $\text{NaOH}$ , both in great dilution, may be represented by the following equation:



or,



The whole reaction is equivalent to the formation of water out of both its ions,  $\text{H}^+$  and  $\text{OH}^-$ , and evidently independent of the nature of the strong acid and of the strong base. The heat of any reaction of this kind must therefore always be the same for equivalent quantities of any strong acids and bases. In reality it is found to be 13,600 cal. in all cases. This thermal equality was the most prominent feature that thermo-chemistry had discovered.

It was now asked in what respect the active state of the electrolytes differs from the inactive one. On this question I gave an answer in 1887. At that time van't Hoff had formulated his wide-reaching law that the molecules in a state of great dilution obey the laws that are valid for the gaseous state, if we only replace the gas-pressure by the osmotic pressure in liquids. As van't Hoff showed, the osmotic

pressure of a dissolved body could much easier be determined by help of a measurement of the freezing point of the solution than directly. Now both the direct measurements made by De Vries, as also the freezing points of electrolytic solutions, showed a much higher osmotic pressure than might be expected from the chemical formula. As for instance the solution of 1 gram-molecule of ethylic alcohol— $C_2H_5OH = 46$  grammes—in one litre gives the freezing-point  $-1.85^\circ C$ , calculated by van't Hoff the solution of 1 gram-molecule of sodium chloride— $NaCl = 58.5$  grammes—in one litre gives the freezing-point  $-3.26^\circ = -1.75 \times 1.85^\circ C$ . This peculiarity may be explained in the same manner as the "abnormal" density of gaseous sal-ammoniac, viz. by assuming a partial dissociation—to 75 per cent.—of the molecules of sodium chloride. For then the solution contains 0.25 gram-molecules of  $NaCl$ , 0.75 gram-molecules of  $Cl$  and 0.75 gram-molecules of  $Na$ , in all 1.75 gram-molecules. Now we have seen before how we may calculate the number of active molecules in the same solution of sodium chloride, and we find by Kohlrausch's measurements precisely the number 0.75. From this I was led to suppose that the active molecules of the salts are divided into their ions. These are wholly free and behave just as other molecules in the solutions. In the same manner I calculated the degree of dissociation of all the electrolytes that were determined at that time—they were about eighty—and I found in general a very good agreement between the two methods of calculation. In a few instances the agreement was not so good, I therefore made new determinations for these bodies and some others; the new determinations were all in good conformity with the theoretical prevision.

The next figure (Fig. 6) shows the freezing-points of some solution of salts, and of non-conductors. As abscissa is used the molecular concentration of the bodies, as ordinates the molecular depression of the freezing-point, divided by 1.85, that should be expected if no dissociation took place. As the figure shows, all the curves for the non-conductors—in this case cane-sugar, propyl-alcohol and phenol—converge towards unity with diminishing concentration. At higher concentrations there occur deviations from the simple law. As examples of binary electrolytes are chosen  $LiOH$ ,  $NaCl$  and  $LiCl$ —their curves all converge towards the number 2. As ternary electrolytes are chosen  $K_2SO_4$ ,  $Na_2SO_4$ ,  $MgCl_2$ , and  $SrCl_2$ , they are decomposed into three ions, and their curves therefore all converge towards the number 3.

As I had taken a step that seemed most adventurous to chemists, there remained to investigate its chemical and physical consequences. The most general and wide-reaching of these is that the properties of a highly attenuated solution of an electrolyte ought to be additive, that is composed of the properties of the different ions into which the electrolyte is decomposed. This was already known to be the case in many instances, and Valson had to this end tabulated his "modules" by the addition of the one value for the negative to the other for

the positive ion, we may calculate the properties of any electrolyte composed of the tabulated ions. In this way we may treat the specific weight (Valson), the molecular conductivity (law of Kohlrausch), the internal friction (Arrhenius), the capillarity (Valson), the compressibility (Röntgen and Schneider), the refractive index (Gladstone), the natural rotation of polarisation (law of Oudemans), the magnetic rotation of polarisation (Perkin and Jahn), the magnetisation (Wiedemann), and all other properties of the electrolytes hitherto sufficiently studied.

The most important of these additive properties are those of which we make use in chemical analysis. As is well known it is generally true that chlorides give a white precipitate with silver salts. It was said formerly that silver salts are reagents for chlorine. Now

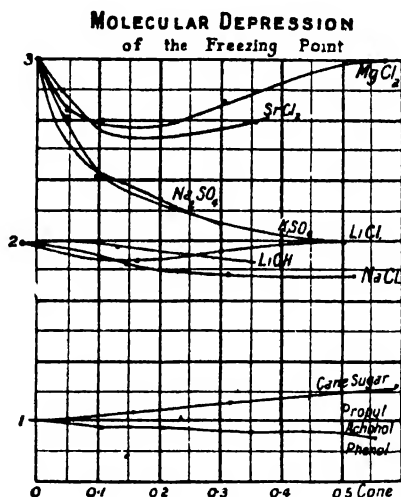


FIG. 6

we say that silver ions are reagents for chlorine ions. This expression is better than the old one, for neither all silver salts e.g. potassium silver cyanide and many other compounds of silver nor all chlorine compounds, e.g. potassium chlorate and many organic chlorides, give this characteristic reaction. The experiment succeeds only with such silver and chlorine compounds as are in a measurable degree decomposed into silver and chlorine ions. Ostwald has treated this question comprehensively, and in this way he has given a rational exposition of the general phenomena of analytical chemistry. To this fact belongs, also, the poisonous effect of some salts; this effect may be considered as a special physiologically chemical reaction of the chemical compounds. On this point there are many valuable researches by Krönig and Paul, Clarke and others.



A property that is of physical character, but is much used by the analytical chemist, is the colour of the solutions. It has been subjected to a rigorous research by Ostwald. At first we will trace how a compound, e.g. fluoresceine,  $H_{12}C_{20}O_5$ , behaves if one replaces its hydrogen atoms by other atoms, e.g. metals, iodine, bromine or atomic groups ( $NO_2$ ). The curves in the next figure (Fig. 7) indicate absorption-bands in the spectra of the corresponding compounds. A replacement of  $K_2$  for  $H_2$  in the fluoresceine itself alters the absorption-spectrum in a most sensible manner. This depends upon the property that the fluoresceine is dissociated to a slight extent, which is in strong contrast to the permanganic acid which will be discussed immediately. Instead of a single absorption-band in the blue in the first case, we find two absorption-bands in the blue-green and the green part of the spectrum for the second. A similar observation

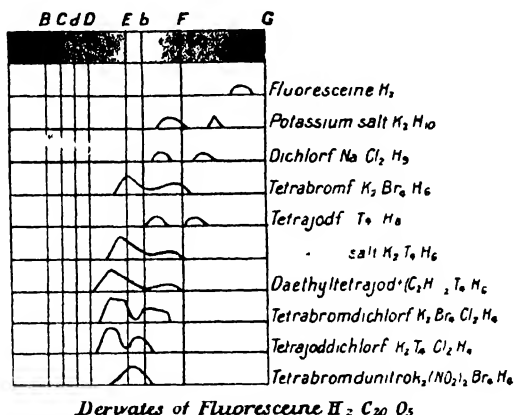


FIG 7

may be made for the tetraiodine-fluoresceine and its potassium salt. In general the figure shows that the spectrum is changed in a very conspicuous manner at the smallest chemical change of the molecule.

It might therefore be expected after the old manner of view, that the replacement of hydrogen by a metal in permanganic acid, or of one acid rest by another in the salts of para-rosaniline would wholly change the character of the spectra. This is not the case, as Ostwald has shown. The spectra are wholly unchanged, as Figs. 8 and 9 show. The spectra are all produced by the same substance, viz., the permanganate-ion in the one, the para-rosaniline-ion in the other case. Only in the case of the para-rosaniline salts we observe that the absorption is sensibly weaker in some cases than in others. The weakening depends upon the hydrolysis of the salts of the weak acids, e.g. acetic and benzoic acids. This research of

Ostwald shows in a most convincing manner the correctness of the views of the theory of electrolytic dissociation.

It has been objected to this theory, that according to it it might be possible by diffusion to separate both ions, e.g. chlorine and sodium, from another in a solution of sodium chloride. In reality chlorine diffuses about 1.4 times more rapidly than sodium. But the ions carry their electric charges with them. Therefore if we place a solution of sodium chloride in a vessel and we pour a layer of pure water over it, it is true that in the first moments a little excess of chlorine enters the water. By this the water is charged negatively, and the solution under it positively, so that the sodium

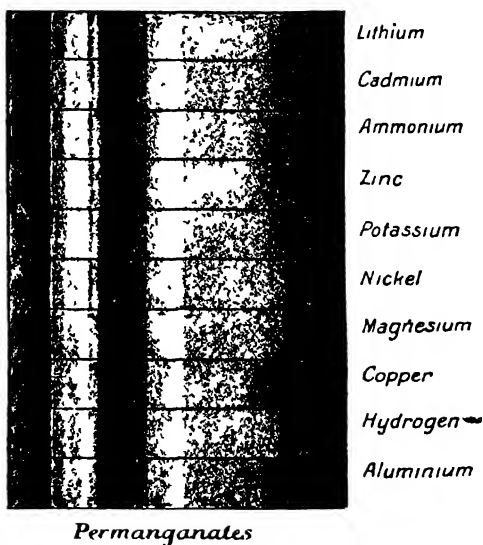
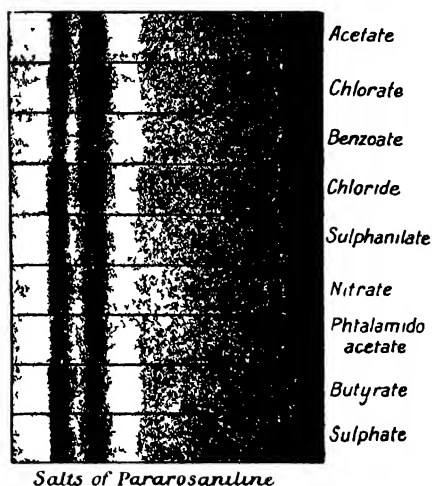


FIG. 8

ions are driven out from the solution with a greater force than the chlorine ions. As soon as that force is 1.4 times greater than this, the chlorine ions travel just as slowly as the sodium ions. It is not difficult to calculate that this case happens as soon as the chlorine ion is contained in the water in an excess of about the billionth part of a milligramme over the equivalent quantity of sodium. This extremely minute quantity we should in vain try to detect by chemical means. By electrical means it succeeds pretty well, as Nernst has demonstrated experimentally for his concentration elements. Therefore, the said objection is valid against the hypothesis of a common dissociation of the salts, but not against a dissociation into ions, that

are charged with electricity, as Faraday's law demands. Probably this objection has hindered an earlier acceptance of a dissociated state of the electrolytes, to which, for instance, Valson and Bartoli inclined.

The gaseous laws that are valid for dilute solutions, have made the calculation of the degree of dissociation possible in a great number of cases. The first application of that nature was made by Ostwald, who showed that the dissociation equilibrium between the ions and the non-dissociated part of a weak acid obeys very nearly the gaseous laws. The same was afterwards demonstrated to be true for weak bases by Bredig. The strongly dissociated electrolytes, chiefly salts, exhibit even in dilute solutions (over 0.05 normal)



*Salts of Pararosaniline*

FIG 9

anomalies, that are not yet wholly explained. Professor Jahn, of Berlin, is at work upon this most interesting question.

— The equilibrium between a greater number of electrolytes has been investigated by myself, and found to be in good agreement with the theoretical previsions. This section includes the questions on the weakening of an acid by addition of its salts, and on the so-called avidity of the different acids, that is, the proportion in which two acids divide a base at partial neutralisation. Calculation gives very nearly the numbers observed experimentally by Thomsen and Ostwald. For heterogeneous equilibria between electrolytes the theory is worked out by van't Hoff and Nernst, who have in this way elucidated the common method to precipitate salts used in analytical chemistry.

By help of the gaseous laws it is also possible to determine the heat evolved at the dissociation of a weak acid or base, and in this way I was able to calculate the heat of neutralisation of acids and bases in a general manner. In an analogous way, Fanjung calculated the changes of volume at dissociation of a weak acid or base and at the neutralisation of these bodies. All these calculations gave values very nearly agreeing with the observed ones.

An important rôle is played by the water, which may be regarded as a weak acid or base. By its electrolytical dissociation, it causes the hydrolysis of salts of weak acids and bases. By observation of the hydrolysis, it was possible to calculate the electrolytic dissociation of water, and this quantity was soon after determined by electrical measurements by Kohlrausch and Heydweiller in perfect agreement with the previous calculations. For physiological chemistry this question is of the greatest importance, as is confirmed by the experimental results of Sjögqvist and others. Also for the explanation of volcanic phenomena, the concurrence between water and silicic acid at different temperatures has found an application.

The catalytic phenomena in which acids and bases are the chief agents, have been investigated by many observers, and it has been found that the catalytic action depends on the quantity of free hydrogen or hydroxyl ions that are present in the solution. To this review, that makes no pretension to be complete, may also be added the wide-reaching researches of van't Hoff, Ostwald, and especially Nernst, on the electromotive forces produced by the ions. By these investigations we have now acquired an explanation of the old problem of the manner in which electromotive forces in hydro-electric combinations are excited.

I have now traced the manner in which the idea of electrolytic dissociation grew out of our old conception of atoms and molecules. Sometimes we hear the objection that this idea may not be true, but only a good working hypothesis. This objection, however, is in reality no objection at all, for we can never be certain that we have found the ultimate truth. The conception of molecules and atoms is sometimes refuted on philosophical grounds, but till he has got a better and more convenient representation of chemical phenomena, the chemist will no doubt continue to use the atomic theory without scruple. Exactly the same is the case for the electrolytic dissociation theory.

This theory has shown us that in the chemical world the most important rôle is played by atoms or complexes of atoms, that are charged with electricity. The common tendency of scientific investigation seems to give an even more preponderating position to electricity, the mightiest agent of Nature. This development is now proceeding very rapidly. Already we see not only how the theory of electrons of J. J. Thomson, in which matter is reduced to a very insignificant part, is developing, but also how efforts are made with

good success to explain matter as only a manifestation of electro-dynamic forces (Kaufmann-Abraham).

To these modern developments the work of British men of science has contributed in the most effective manner. The bold previsions of Sir William Crookes seem to be rapidly acquiring a concrete form, to the great benefit of scientific evolution.]

[S. A.]

Friday, January 20, 1905.

LUDWIG MOND, Esq., Ph.D. D.Sc. F.R.S., Vice-President,  
in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*

*New Low Temperature Phenomena.*

THE porosity of matter, and the possibility of the occlusion of gases in it, has been the subject of scientific thought for ages. As early as 1674, Boyle,\* under the title "Suspensions about the hidden Qualities of Air," writes: "It may not seem altogether improbable, that some bodies we are conversant with, may have a peculiar disposition and fitness to be wrought on by, or to be associated with, some of those exotic effluvia that are emitted by unknown bodies lodged underground, or that proceed from this or that planet. . . . We may be allowed to consider whether among the bodies we are acquainted with here below, there may not be found some that may be receptacles, if not also attractives, of the sidereal and other exotic effluvia that rove up and down in our air." While other matters took up his immediate attention, this one was not lost sight of, for ten years later, in 1684, he returns to the subject in a special discourse. "Experiments and considerations about the porosity of Bodies,"† in which he says: "When I consider how much most of the qualities of bodies, and consequently their operations, depend upon the structure of their minute and singly invisible particles, and that to this latent contexture, the bigness, the figure, and the collocation of the intervals and pores do necessarily concur with the size, shape and disposition, or contrivance, of the substantial parts, I cannot but think the doctrine of the small pores of bodies of no small importance to Natural Philosophy." Felix Fontana, the famous physicist to Duke Ferdinand II. of Tuscany, seems to have been the first to have discovered the absorptive power of hot charcoal for gases, a property which he communicated to Priestley, about 1770, and which Priestley confirmed. Lowitz, in 1791, noticed that charcoal decolorised organic solutions. Later experiments were made by Morozzo, and another series of observations were made by two Dutch physicists, Romppe and Norden. Shortly after this, early in last century, the subject of the action of gases on charcoal was elaborately examined by Theodore

\* Boyle, Works, vol. iii., p. 470, col. 1.

† Boyle, Works, vol. iv., p. 206, col. 1.

de Saussure. Subsequently Graham and Stenhouse added valuable contributions to the inquiry. The thermal evolutions of some gaseous absorptions in charcoal were determined by Faure and Silbermann; and later, Hunter showed the advantage of using cocoa-nut charcoal, and made a long series of investigations on the absorption of organic vapours and gases by this variety of charcoal.

In de Saussure's experiment a piece of red-hot charcoal was plunged under mercury, and introduced into the gas to be absorbed after it was cool, without allowing it to come in contact with air. He made use of box-wood charcoal, about which he remarks that it absorbed so little mercury during the cooling that it would readily swim on water. His experiments were conducted at ordinary temperature and pressure, and gave the results in the annexed table, the unit volume being that of the absorbing charcoal. For comparison, similar experiments made by Hunter with cocoa-nut charcoal are given.

	Boxwood (Saussure)	Cocoa-nut (Hunter)
Ammonia .. .. .	90	172
Hydrochloric acid .. .	85	—
Sulphurous acid .. .	65	—
Sulphuretted hydrogen ..	55	—
Nitrous oxide .. .	40	86
Carbonic acid .. .	35	68
Olefiant gas .. .	35	75
Carbonic oxide.. .	9.42	21
Oxygen .. .	9.25	18
Nitrogen .. .	7.5	15
Hydrogen .. .	1.75	4

He found that even if the charcoal were moistened with water, it was still capable of absorbing one-third to one-half the amount of gas absorbed when quite dry.

During these experiments he called attention to the evolution of heat during absorption, and remarked that it appeared to increase with the absorbability of the gas.

In further experiments he considered the effect of pressure on the amount of absorption, and found that absorption by volume is far greater in a rare than in a dense atmosphere, but that if reckoned by weight it is more considerable in the latter than in the former state.\*

He continued similar experiments with meerschaum, asbestos, and other substances, and also examined the effect of mixed gases.

Hunter examined the absorption of vapours by cocoa-nut charcoal at or above their boiling points with interesting and suggestive results

\* Saussure's results for carbonic acid may be represented by the formula—

$$v = 15.3 + \frac{551.7}{p}$$

$$v = 19.1 + .53 p;$$

where  $v$  is the volume absorbed, measured as above, and  $p$  is the pressure in inches of mercury.

as regards selective action. The following table is a selection made from some of his observations :—

COCOA-NUT CHARCOAL ABSORPTION OF VAPOURS AT BOILING POINT  
OF LIQUID (HUNTER).

Carbon tetrachloride	.. .. .	4
Chloroform	.. .. .	30
Ethyl iodide	.. .. .	86
Alcohol	.. .. .	141
Benzol	.. .. .	59
Carbon bisulphide	.. .. .	117
Ether	.. .. .	87
Ethylamine	.. .. .	127
Water	.. .. .	55

In a note read before the Royal Society of Edinburgh in March 1874, connected with a research undertaken in association with the late Professor Tait, the absorptive power of charcoal was employed for the first time in the production of high vacua. A piece of cocoa-nut charcoal was placed in a glass tube, into which were sealed two platinum terminals for electric sparking. The tube was exhausted by the mercury pump, while the charcoal was at the same time heated to a red heat. On sealing off the tube, and allowing the charcoal to cool, the vacuum was so perfect that no spark would pass between the terminals, from a coil giving quarter-of-an-inch sparks in air. Similar experiments were repeated when investigating the theory of the motion of the Crookes Radiometer, and are detailed in "Nature" in 1875.

One advantage of charcoal vacua in the study of electric discharges is that on heating the charcoal slowly, and connecting the platinum terminals to the induction coil, the *stræ* may be reproduced and maintained at any degree of rarefaction desired, and as often as we please.

At the Conference on May 24, 1876, in connection with the Loan Collection of Scientific Apparatus at South Kensington, I showed a further simplification and advance in the production of high vacua. A little fluid bromine was placed in a tube, and the tube was put in a water bath, so that the bromine boiled off. Meanwhile the charcoal in another part of the tube was heated in the usual way, and when all the bromine had been vaporised the tube was sealed off. On the charcoal cooling it absorbed the bromine so thoroughly that no trace of colour was visible. In this way a vacuum is produced without the use of any exhausting pump.

Although all charcoals exhibit absorptive powers of a high order, nevertheless differences are noticeable. Among charcoals got from wood, the denser woods seem to produce the more absorptive charcoals. Thus box-wood charcoal is more absorptive than fir-charcoal. Saussure found the following relative absorptive powers from different wood charcoals :—

	Sp. gr.	Absorption.
Cork .. .. .	0.1	Imperceptible.
Fir .. .. .	0.4	4½ its vol. of air.
Boxwood .. .. .	0.6	7½ "
Russberg coal (vegetable origin)	1.3	10½ "



But at last the porosity must become so fine that absorption again disappears. Thus Cumberland black lead (which is 96 per cent. carbon), of sp. gr. 2·17, showed no absorption.

From experiments, detailed on a former occasion,\* undertaken to determine the effect of various substances in a state of fine division placed within the walls of vacuum vessels in protecting the contents of the vessels from external heat, by reason of bad thermal conductivity and the interference of the mean free path of the gas molecules, I found that charcoal and lampblack were nearly equally good at the temperature of liquid air, and that each was four times as good as graphite.

From some recent investigations I find that charcoals so different in their origin as cocoa-nut charcoal and charcoal from cane-sugar differ but little in their absorptive powers for a gas like hydrogen.†

Mitscherlich specially studied the nature of porosity in connection with the occlusion of gases. Taking a piece of charcoal weighing 0·9565 gm., and thoroughly saturating it with water, he found that it weighed 2·2585 gm. in air, and 0·110 gm. under water. Hence of the gross volume of the charcoal,  $\frac{3}{4}$  was occupied by charcoal substance, and  $\frac{1}{4}$  was free space into which gases might be absorbed. Saussure found that charcoal at 12° C. and ordinary pressure absorbed 35 times its volume of carbonic acid, but as this occupied  $\frac{2}{3}$  of the gross volume of the charcoal, it was actually forced into a space equal to only  $\frac{1}{3}$  of its original volume. He concluded, therefore, that about a third of the gas was liquefied in the pores of the charcoal.‡

He found that the cells of charred wood are on an average  $\frac{1}{100}$  of an inch in diameter. Now, if a cubic inch of charcoal were cut up into a number of small equal cubes each of whose edges was  $\frac{1}{100}$  inch, the total area of their surfaces would be 100 square feet, or taking into account the space occupied by the charcoal itself, it would leave about 73 square feet. The thickness of the liquefied carbonic acid over this area would, then, be about ·000002 inch.

This harmonises to a certain extent with Saussure's remark that denser charcoals, that is, charcoals with pores of smaller diameters,

\* Liquid Air as an Analytic Agent, Roy. Inst., 1 Ap., 1898.

† Approx. Series of 30/10/04, range 250 c.c. to 2750 c.c., gave  
log.  $p = -\cdot 08 + \cdot 267$  c. Cocoa-nut.

Series 4/11/04, range 250 c.c. to 2250 c.c., gave  
log.  $p = \cdot 39 + \cdot 195$  c. Cane-sugar.

If  $p = 100$  mm., these give respectively

$$c. = \frac{2\cdot08}{\cdot 267} = 7\cdot8. \text{ Cocoa-nut;}$$

$$\text{and } c. = \frac{1\cdot61}{\cdot 195} = 8\cdot3. \text{ Cane-sugar.}$$

‡ From Amagat's observations, the amount liquefied was almost exactly one-fifth.

and representing a greater surface for condensation, are the greater absorbers. Nevertheless, we must not forget to notice that the affinities between charcoal and different gases are not the same, and that these will seriously modify any results derived from mere geometrical considerations.

*Thermal Evolution and Absorption of Gases by Charcoal  
at Low Temperatures.\**

Saussure first observed and roughly noted that the absorption of gases by charcoal at the ordinary temperature gave rise to a considerable evolution of heat. The liquid air and hydrogen calorimeters can be easily arranged to afford an exact measure of the quantities of heat thus given up by the condensation of different gases in charcoal. For this purpose a small glass bulb C, contain-

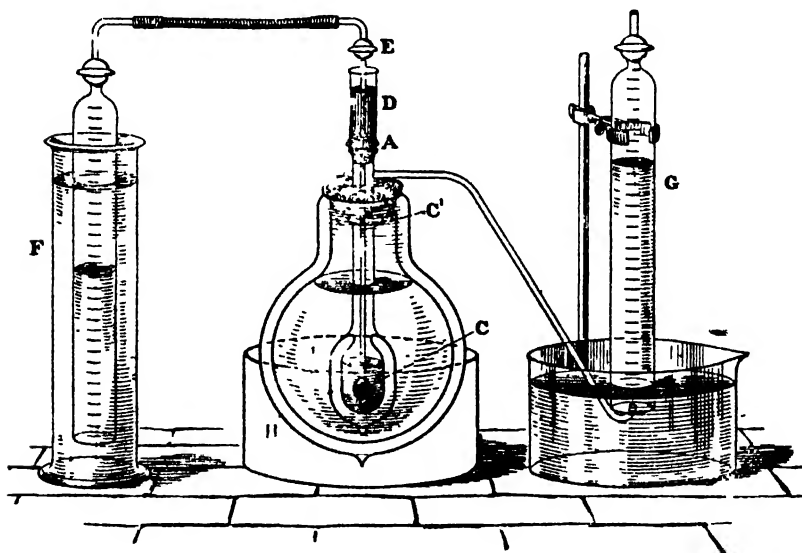


FIG. 1.

ing from half a gramme to a gramme of charcoal, has a long narrow tube C' attached, so that it can be immersed in the liquid oxygen, or air in the calorimeter A B, while still allowing a part of the tube to project above the cork A. The calorimeter is then inserted in a large vacuum vessel H, containing two or three litres of liquid oxygen or air, as the case may be, and kept in its place by a loose stuffing of cotton wool. In order to dry and cool the entering gas (which, in my experiments, did not exceed

\* Proc. Roy. Soc., 1904. 3

40 c.c.), a little annular space is arranged at D, into which liquid air is poured immediately before the experiment begins.

The charcoal, after being placed in the small bulb C, is heated to a low red heat, and simultaneously exhausted by a good air-pump, and after all the gas has been removed, the stop-cock E is closed. In this condition it is placed in the calorimeter B.

The experiment is conducted by connecting the end of the tube at E by means of an indiarubber tube with the graduated vessel F containing the gas to be examined. When all is ready the stop-cock E is opened, so that the gas may rush into the charcoal, and the heat evolved by its absorption distils off the equivalent quantity of liquid air from the calorimeter B, which is then received and measured in the vessel G.

When we know the constant of the calorimeter—namely, the number of cubic centimetres of gas evaporated by one calorie (about 14·5 c.c. in the present case)—from the readings of the two jars F and G we find at once the heat evolved in the condensation per unit volume of gas absorbed. After making a few necessary corrections, the results for different gases are as given in the following table :—

	I. Volume absorbed at 0° C	II. Volume absorbed at - 185° C.	III. Ratio of II. to I.	IV. Heat evolved in gramme calories by absorption at - 185° C.
Helium .. .. .	2 c.c.	15 c.c.	7·5	2·0
Hydrogen .. .. .	4 "	135 "	34·0	9·3
Electrolytic gas .. .. .	12 "	150 "	12·5	17·0
Argon .. .. .	12 "	175 "	14·6	25·0
Nitrogen .. .. .	15 "	155 "	10·3	25·5
Oxygen .. .. .	18 "	230 "	12·8	34·0
Carbonic oxide .. .. .	21 "	190 "	9·0	27·5
Carbonic oxide and oxygen ..	30 "	195 "	6·5	34·5

To render these results comparable, the same specimen of coconut charcoal was used for them all, and the numbers in the last column are for absorption by one gramme of charcoal. The volumes of the gases absorbed are, both at ordinary and low temperatures, given under standard conditions—namely, 0° C. and 760 mm. of mercury pressure. If it is desired to know the volumes absorbed at - 185° C., when these volumes are measured at - 185° C. and 760 mm. pressure, we have only to divide the numbers in column II. by three.

In each case, a very remarkable increase of absorption takes place at the low temperature. This is shown in column III. It is further remarkable that the increase of absorption diminishes, roughly, as the boiling points of the various gases increase, while column IV. shows a corresponding increase in the quantities of heat evolved.

The general results are seen best when the values of the thermal evolution and the amount of charcoal involved are reduced to molecular volumes of the condensed gas.

### *Heat Evolution.*

#### Charcoal absorption per Molecular Volume.

	Calories.	Wght. of Charcoal.
Hydrogen .. .. .	1600	206 grms.
Nitrogen .. .. .	3686	180 "
Argon .. .. .	3686	162 "
Oxygen .. .. .	3744	160 "
Carbonic Oxide .. .. .	3416	148 "
Carbonic Oxide and Oxygen .. .. .	3960	144 "
Electrolytic Gas .. .. .	2414	180 "

Mean  $C_{11}M$ ; limit  $C_8H_2$  and  $C_{12}He$ .

A comparison of the molecular latent heats of the liquefied gases, hydrogen, nitrogen and oxygen, with the charcoal heat of condensation in each case, is shown in the following table:—

	Molecular Latent Heats. (Calories)	Molecular Absorption in Charcoal. (Calories)
Hydrogen .. .. .	238	1600
Nitrogen .. .. .	1372	3684
Oxygen .. .. .	1664	3744

But perhaps the most striking result is the great difference in properties exhibited by helium. While resembling other cases in showing increased absorption at the temperature of liquid air, the absolute amount occluded is about one-tenth that of the other gases at the same temperature, and the quantity of heat evolved is in even a smaller ratio. We must, however, note that the position of helium on the scale of temperatures, for these experiments, is quite different from that of the other gases, even hydrogen. For helium is being absorbed at a temperature some fifteen times higher than its boiling point (say  $6^\circ$  abs.), while in the case of hydrogen this is only four-and-a-half times its boiling point ( $20^\circ$  abs.). To make a fair comparison, we should take hydrogen at fifteen times its boiling point, which would bring us up to some  $27^\circ$  C., that is, the helium absorption at  $-185^\circ$  C. should preferably be compared with the hydrogen absorption at  $0^\circ$  C. The inference then is, that if we had the absorption of helium at  $25^\circ$  to  $30^\circ$  absolute, we should find it show a still more remarkable condensation than hydrogen does at  $90^\circ$  abs. ( $-183^\circ$  abs.).

The following experimental results confirm this point of view:—

### *Helium and Hydrogen.*

#### Charcoal Absorption at the Temperatures of Boiling and Solid Hydrogen.

Temperature.	Helium. Vols. of Carbon.	Hydrogen. Vols. of Carbon.
$-185^\circ$ C. (boiling point of liquid air)	$2\frac{1}{2}$	137
$-210^\circ$ C. (liquid air under exhaustion)	5	180
$-252^\circ$ C. (boiling point of liquid hydrogen)	160	258
$-258^\circ$ C. (solid hydrogen)	195	

As the relation between volume and temperature is nearly lineal at the lowest portions of either the hydrogen or helium absorption, we may infer that at the temperature of from  $5^{\circ}$  to  $6^{\circ}$  helium would be as freely absorbed by charcoal as hydrogen is at its boiling point, and that in all probability the boiling point of helium is not below  $5^{\circ}$  abs. This inference is quite legitimate, because good charcoal at the respective boiling points of liquid hydrogen, nitrogen or oxygen, absorbs at atmospheric pressure nearly the same volume of each gas, viz., 260 c.c. per gramme.

It is to be noted that the rate of increase of the helium absorption is three times that of the hydrogen, so that a degree or two makes a large increase in the volume condensed. From these results it seems highly probable that the boiling point of helium is about a fourth that of hydrogen, just as the latter is about one-fourth that of nitrogen.

In column IV. we get the heat evolved by each gas. These values provide us with still further striking results, for the heat developed is, generally, greatly in excess of that required for liquefaction. Thus, for hydrogen, whose latent heat at the boiling point I have recently determined by this calorimeter and found to be 120 gramme calories, the liquefaction of 135 c.c. of this gas would only evolve about  $1\frac{1}{2}$  calories, or  $\frac{1}{40}$ th of that evolved by occlusion in charcoal at the boiling point of air. Similarly, if we take 51 gramme calories as the latent heat of oxygen, the liquefaction of 230 c.c. of this gas would produce some 17 calories, or about half of that evolved during occlusion.

#### *Separation of Highly Concentrated Oxygen from Air by Charcoal at Low Temperatures.*

In order to examine the changes taking place in a mixed gas like air during the absorption, a quantity of about 50 grammes of charcoal was after heating and absorption saturated at  $-185^{\circ}$  in a current of pure dry air—got by passing the air current through a U-tube immersed in liquid air.

For a time the air rushed into the charcoal with great rapidity, and in about 10 minutes between 5 and 6 litres were taken in. A manometer attached to the vessel containing the charcoal showed, on shutting off the air current, that during the early part of the saturation the absorption was so effective as to give practically no measurable mercury pressure. As soon as the absorption was ended, and a current began to pass slowly over the charcoal, the composition of the air leaving the charcoal showed 98 per cent. nitrogen. After the current of air had passed for half an hour, the total gas occluded in the charcoal was expelled by taking the vessel in which it had been treated out of the liquid air, and allowing the temperature to rise to  $15^{\circ}$  C.

The gas, which was rapidly expelled, measured 5.7 litres, and contained 56 per cent. of oxygen. If the saturated charcoal before heating was subjected for an hour to the action of an air-pump, capable of giving a steady exhaustion of 5 mm., no difference was effected in the oxygen percentage of the evolved gas. The same experiment was repeated with this variation, that, instead of the air current having the pressure of the atmosphere, it was kept below one-tenth of an atmosphere. In this experiment 4.8 litres were expelled on heating up, and the percentage of oxygen was 58. Then, a further repetition was made with an air current supplied at a pressure not exceeding 5 mm. of mercury. After 3 hours' treatment, the charcoal, on heating to 15° C., gave 4½ litres of 57 per cent. oxygen. From these experiments it follows that the tension of the occluded gases, at the temperature of liquid air, must be very small, and thus the use of low temperatures, combined with charcoal, introduces a new and greatly improved means of getting high vacua, which in the future may be found susceptible of important practical applications. These experiments are quite conclusive as to the practical constancy of the mean composition of the air gases occluded in the charcoal (subject to the conditions aforesaid), and they further show that wide changes in the pressure of the air current has little or no effect in altering the proportions. In another experiment, the vessel containing the saturated charcoal, instead of being allowed to rise rapidly in temperature, was transferred to a vacuum vessel, in which a little liquid air was placed, in order that the temperature might rise slowly, and thereby enable the successive litres of gas given off to be collected separately and analysed.

This experiment gave the following results :—

	Oxygen per cent.
First litre .. . . .	18.5
Second „ .. . . .	20.6
Third „ .. . . .	53.0
Fourth „ .. . . .	72.0
Fifth „ .. . . .	79.0
Sixth „ .. . . .	84.0

The mean composition of the 6 litres is again 56 per cent. oxygen. From the above experiments it follows that one of the most rapid means of extracting a high percentage of oxygen from atmospheric air is to absorb it in charcoal at low temperatures, and thus to expel it either rapidly or slowly by heating the mass of charcoal to the ordinary temperature.

A few experiments have been made using, instead of air, special mixtures of oxygen and nitrogen. Thus it was found that a gas containing 6.5 per cent. of oxygen, used in the same manner as in the air occlusion experiments, gave, on heating up the charcoal rapidly to 15° C., 5 litres of gas having the composition of 23 per cent. of oxygen. A repetition of the same process with the 23 per cent. of oxygen would have raised the percentage about 60 per cent., or a stronger

concentration could have been reached by fractionating the gas as it slowly leaves the charcoal on gradually increasing the temperature.

*Production of High Vacua and Spectroscopic Studies. Separation of Gases like Helium, Neon, and Hydrogen, from Air and other Gas Mixtures.\**

The high absorption of gases by charcoal suggested an inquiry into the limits of gaseous pressure reached by such means of condensation. With this object, an ordinary spectroscopic sparking tube A B was sealed to a narrow tube C E, the end of which was blown into a bulb, D E, capable of containing a few grammes of cocoanut charcoal. After the charcoal had been freed from gases by heating and exhaustion, and the poles cleared by sparking during this operation, pure and dry gases like oxygen, nitrogen, air, carbonic oxide, hydrogen, neon, and helium, could be admitted at different pressures and the tube with its attached charcoal chamber sealed off.

On placing the charcoal capsule in liquid air, the gas in each case was rapidly absorbed, and the vacuum produced reached the phosphorescent stage, except in the cases of hydrogen, neon, and helium.

A large spectroscopic tube of 1300 c.c. capacity was sealed to a bulb containing 30 grammes of charcoal. When the tube was filled with air at atmospheric pressure and the charcoal cooled in liquid air, the pressure fell to 50 mm. of mercury. On refilling the tube with air at the pressure of half an atmosphere, and treating it as before, the exhaustion reached beyond the striæ stage; and a final charge at a quarter of an atmosphere gave a vacuum through which no spark passed. When the experiment was repeated with only 1 gramme of charcoal, and an initial pressure of 3 mm. of mercury, the vacuum just reached the beginning of the phosphorescent stage.

When hydrogen was employed, in order to get a vacuum well up in the striæ stage, either a larger amount of charcoal had to be employed or the initial pressure had to be less than an atmosphere. But, if the liquid air bath was cooled to  $-210^{\circ}\text{C}$ . by exhaustion, the tube just reached the beginning of phosphorescence round the cathodes. With helium there was very slight absorption, but more appreciable results were obtained with neon. Spectroscopic observations made during the condensation of the gas in the charcoal showed the gradual disappearance of the characteristic spectrum of oxygen, nitrogen, and air, as the high vacuum was reached and the discharge passed with great difficulty. In tubes of this kind filled at atmo-

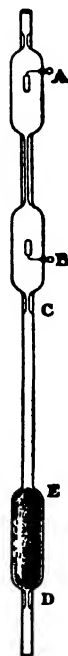


FIG. 2.

\* Proc. Roy. Soc., 1904.

spheric pressure, the F line of hydrogen and the neon yellow could always be seen; but the helium was not seen with any definiteness. As the amount of neon in the air cannot well exceed  $\frac{1}{100000}$ th, the spectroscopic test is very delicate.

In order to get the helium spectrum the air in the sparking tube had to be enriched six or seven times. This was attained by the apparatus in Fig. 3. A B is the sparking tube, with its small charcoal bulb C attached, capable of being sealed off at G when required; and D and E are larger charcoal absorbers placed in vacuum tubes containing liquid air; the whole being attached to a graduated gas-holder, F, containing air. A series of glass stop-cocks are attached at the points H, I, J, and K, to facilitate manipulation.

In a preliminary experiment to determine the volume of air necessary to bring in the helium lines, 200 c.c. of air were supplied to one of the charcoal vessels D, containing 15 grm. of charcoal, from which the residue was passed on to the sparking tube. This tube gave the hydrogen lines C and F, the neon yellow and some of

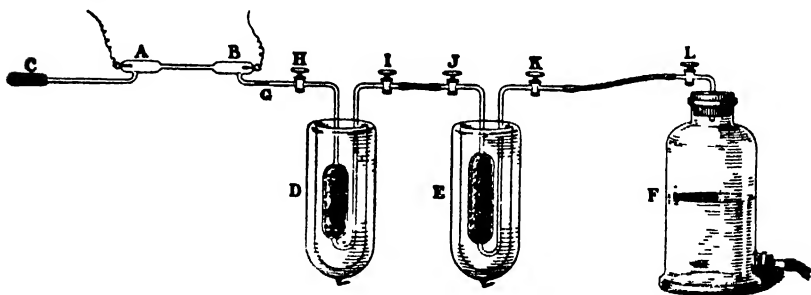


FIG. 3.

the orange lines, along with the helium yellow and green quite distinctly. Another tube with the residuary gas from a litre of air gave all the helium lines as well as the neon yellow and the hydrogen F; from which we infer that by this means  $\frac{1}{100000}$ th of helium can be detected, so that the test is as delicate for helium as for neon. A third tube, supplied from 3 litres of air, gave the neon and helium spectra and a brilliant ruddy glow discharge.

As 40 to 50 grammes of charcoal can absorb at the temperature of liquid air from 5 to 6 litres of air, it is easy to accumulate rapidly the uncondensed gases in considerable quantities for spectroscopic examination. For this purpose it is convenient to use two charcoal condensers in circuit. After the charcoal in the first one, marked E in figure, was saturated, the stop-cock K was closed, while I and J were opened for a short time to allow the less condensable gas in E to be sucked into the second condenser D along with some portion of air. The condenser E was then taken out of the liquid air, rapidly heated to  $15^{\circ}\text{C}$ . to expel the excluded air, and was thus ready to repeat the



operation. In this way 50 litres of air can be treated in a short time, supplying sparking tubes showing brilliantly the complete spectra of the volatile constituents of the air.

The results derived from the treatment of Bath gas in this way are interesting. This gas, consisting mainly of nitrogen and  $\frac{1}{1000}$ th part helium, when subjected to the action of the charcoal condenser in liquid air, gives no high vacuum. All the nitrogen and any other constituents are absorbed, and a spectrum of helium and hydrogen showing much less neon than exists in the volatile residue from atmospheric air is the result. A sample of argon prepared from Bath gas treated in the same way, gives a tube showing the helium and neon spectrum; and one prepared from atmospheric air gives a similar result, but the helium spectrum is the stronger in the Bath argon, whereas with the atmospheric argon the neon spectrum is the most pronounced.

*Illustrations of various Applications of Charcoal in Experimental Investigations.*

The gaseous products from minerals containing helium, hydrogen, etc., also the products from radium compounds, may be treated by the charcoal method. As an example I have applied this method to the crude gases got by heating the mineral Fergusonite. During the cooling of the charcoal the nitrogen and hydrogen spectra were marked, but in a short time nothing could be seen but the lines of hydrogen and helium. It is needless to say that the charcoal method of exhaustion can be applied to the manufacture of incandescent lamps and Röntgen radiation tubes, and that the method can be conveniently employed to produce and maintain high vacuum for the purpose of distilling bodies under low pressures. Many experiments with the radiometer can be carried out by the use of the charcoal method of exhaustion. If a charcoal capsule is sealed to the bulb of a radiometer full of air under relatively high pressure, on directing a beam of light on the vanes of the radiometer they remain at rest, showing that the density of the air is too great for motion to take place. When, however, the charcoal capsule is immersed in a vessel containing liquid air, the vanes immediately commence a rapid rotation. On removing this liquid air bath their motion slackens, and finally they come to rest as the charcoal returns to the temperature of the room.

It is known that dry phosphorus does not enter into chemical combination with pure oxygen at ordinary temperature and pressure. A bulb of from 100 to 200 c.c. filled with pure oxygen, having a side tube sealed on of 2 mm. cross section containing fused phosphorus, the whole being connected by means of a quill tube to a charcoal capsule, containing in part also a good layer of phosphoric anhydride, and the latter immersed in liquid air, the charcoal gradually absorbs

the oxygen, and at a particular pressure the oxydation of the phosphorus vapour begins, and is revealed in the form of a phosphorescent

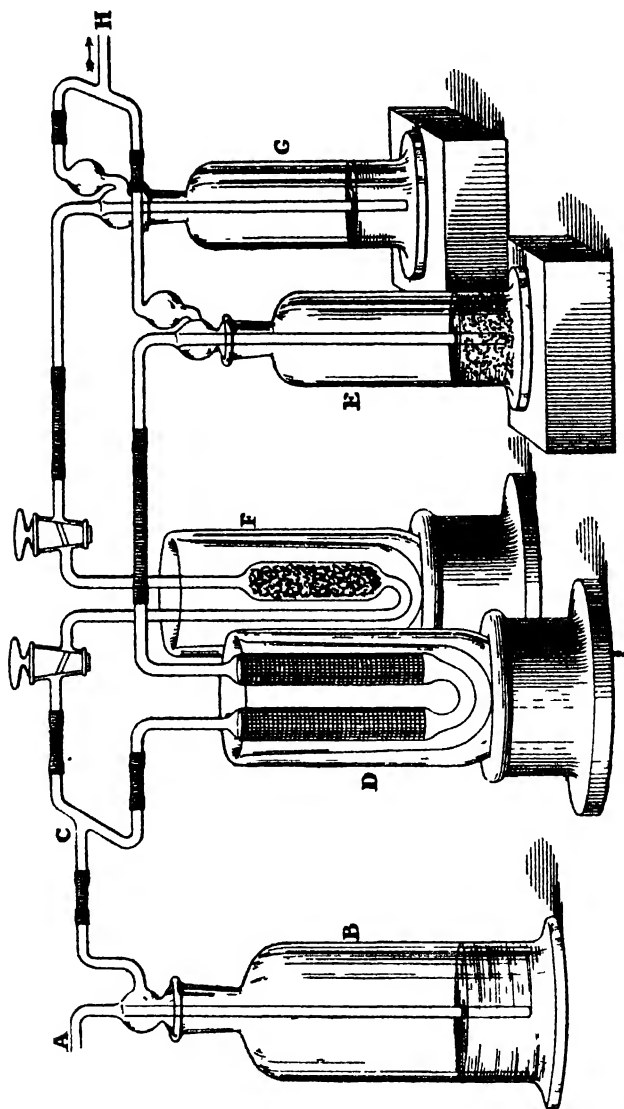


FIG. 4.

glow, filling the whole of the glass bulb, which continues until the oxygen pressure gets too low. On removing the liquid air bath,

at a certain stage of the increasing pressure of oxygen, the bulb again becomes a glowing mass of phosphorescence, which wanes and disappears as the normal pressure is reached. This experi-

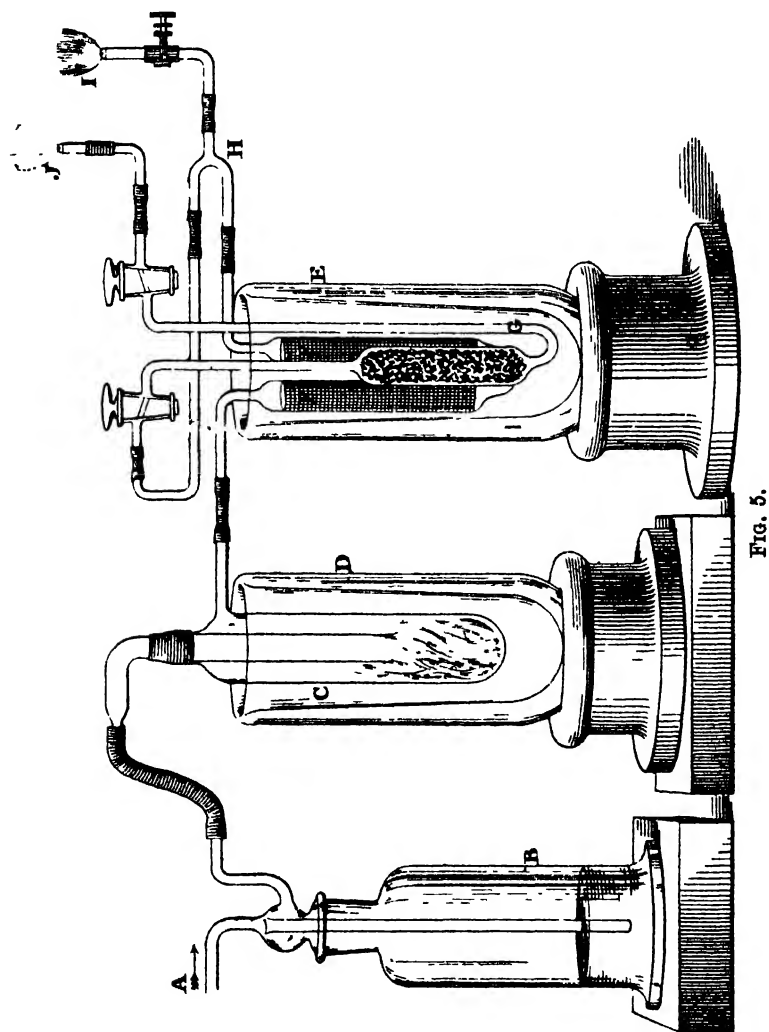


FIG. 5.

ment may be repeated a great many times provided the phosphorus in the small side tube does not get into active combustion, which can always be avoided by a slight cooling. Such bulbs can be

kept in the dark for months, and at the end of the time are quite active when cooled as described. A manometer attached to the side of the oxygen bulb shows that the oxygen pressure at the moment phosphorescence begins is only a fraction of a millimetre of mercury. From these results it appears that perfectly dry oxygen below 1 mm. pressure combines with phosphorus.

The following experiment proving the absorption of carbonic acid, at a small partial pressure, by charcoal is very striking. A continuous stream of ordinary atmospheric air, containing three volumes of carbonic acid in ten thousand, is made to enter the apparatus, Fig. 4, at A and leave at H. It first passes through the jar B, which contains some strong sulphuric acid, by which it is thoroughly dried. On leaving B the stream of air is divided at C into two portions, one of which passes through the jars D, E, the other through the jars F, G, the two finally uniting and passing out at H. D and F are vacuum vessels containing solid carbonic acid, which maintains a temperature of  $-78^{\circ}\text{C}$ . The air passes through a U-tube in D, the arms of which are filled with coils of copper gauze to ensure the complete reduction of its temperature to  $-78^{\circ}\text{C}$ . It next passes through the jar E, containing some baryta water, which absorbs the carbonic acid remaining in it, before it emerges at H. The other stream of air passes in like manner through a U-tube in F, in one arm of which is a quantity of dry charcoal in small lumps; thence, after bubbling through some baryta water in the jar G, it passes to H, where it escapes. Now, the streams of air entering D and F are in exactly the same state, but while E shows by the milky deposit taking place that the one stream is still fully charged with carbonic acid after being thoroughly cooled to  $-78^{\circ}\text{C}$ . in D, G shows by remaining permanently clear that a similar cooling of air to  $-78^{\circ}\text{C}$ . in the presence of charcoal causes, for a time, complete absorption of the carbonic acid from the air, and this goes on until the charcoal absorbs about 1 per cent. of its weight of carbonic acid.

The absorptive power of charcoal for hydro-carbons is shown in a similar manner by the following experiment: common coal gas enters the apparatus in Fig. 5 by the tube at A, and after being dried by bubbling through strong sulphuric acid in the jar B, has the less volatile gases condensed by passing through a vessel C cooled with carbonic acid snow, isolated in the vacuum vessel D. The gas is further purified by percolating through the two copper coils contained in the arms of the U-tube F F, immersed also in solid carbonic acid in the vacuum vessel E, after which it passes on to H, where its path is bifurcated, one branch leading to I, where the issuing gas is lighted, while by the other branch the purified gas passes over charcoal in the U-tube G, also at the temperature of solid carbonic acid, before proceeding to J, where it in turn is lighted. The difference between the two flames is very noticeable, that at I being quite luminous, while the other at J is non-luminous, like a Bunsen flame. The explanation is, that the charcoal at the temperature of  $-78^{\circ}\text{C}$ . completely

absorbs for a time all the hydrocarbons, such as marsh gas and ethylene, upon which the luminosity of the flame of coal gas depends, leaving practically carbonic oxide and hydrogen.

This preliminary investigation suggests many fields for further inquiry, and some of these I hope to deal with in future lectures.

My thanks are due to my chief assistant, Mr. Robert Lennox, F.C.S., for valuable aid in the conduct of the experiments; and Mr. J. W. Heath, F.C.S., has also helped in the progress of the work.

[J.D.]

Friday, February 17, 1905.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. F.R.S., Treasurer  
and Vice-President, in the Chair.

JOHN W. GORDON, Esq., *M.R.I.*

*High Power Microscopy.*

IN the exhibition of a microscopic object under high magnifying power, there are three stages at which difficulties have to be encountered and surmounted.

1. In the preparation of the object for exhibition under suitable conditions of illumination.

2. In the representation of the object by means of an image.

3. In the transmission of the image so formed in the instrument to the eye of the observer.

Dealing first with the preparation of the object. Professor Wright has suggested a classification from this point of view according to which microscopic pictures fall into two classes, which, adopting a nomenclature employed by Professor Koch, he calls colour pictures and outline pictures. A colour picture, as its name suggests, is usually the result of a stain, but its specific character does not depend upon its tint. The distinctive property of a colour picture is that the structure is shown by masses or washes of colour without delineation, whereas in the outline picture the contours are delineated and the masses have the same tone as the background. Fig. 1—a photograph of a piece of lung tissue—is an example of a colour picture. Fig. 2—a photograph of four strands of gossamer—affords an illustration of an outline picture. The colour picture possesses many advantages, especially where measurements are in question, for the single boundary which is the common outline both of the object and of the background, is more easily identified than the more or less nebulous line by means of which an outline picture is delineated. But with a large number of objects the staining method fails altogether, and it is necessary therefore to have recourse to the alternative type of picture. This depends for its formation upon difference of refractive index between the object and the background. The theory is perfectly well known, but may be usefully brought to mind by a simple illustration such as is afforded by Fig. 3. A very close and easily intelligible analogy to the theory of refraction may be found if we assume first that Fig. 3 illustrates

the march of a company of soldiers across a field, part of which—the darkened portion—is covered with grass and affords good foothold, while the light part represents ice across which it is possible to march only with a shortened step. Now assume that the men receive directions to march shoulder to shoulder and straight ahead. The first step will carry the line forward in unbroken formation parallel with itself into the position shown by the second line of men in the diagram, but upon the second step the man of the first file on the left will step short since he steps upon ice. In order to observe the shoulder to shoulder rule he must advance his right shoulder, and for the same reason his right hand man must retire his left shoulder. Upon the third step both the first and the second file men will step short, keeping step with one another, and the second man will have to advance his right shoulder to keep touch with his right hand man, thus completing the half-turn which he commenced by retiring his left shoulder when his left hand man fell behind. At the next step the third man will execute the same evolution, and so, gradually, a new line will form itself upon the ice, breaking off at a definite angle from the line of the original formation. When the farther edge of the ice is reached all these evolutions will be repeated in inverse order, with the result, shown in the diagram, that the column which has passed over the ice marches thereafter, when the farther grass is gained, in a new direction branching away from the unchanged direction of the column which has never left the grass. It is obvious, without detailed discussion, that the extent of the deviation—the angle of refraction—depends upon the change of step at the two boundaries where grass and ice meet, and if the matter were investigated it would be found that the mathematical rule which determines this angle is the rule commonly known as the law of sines, by which the refraction of light is calculated.

To pass from this imaginary march to the analogous case of the progress of a beam of light is quite easy. The successive ranks in the formation, which represent equal distances measured in steps from an original position, or zero line, correspond to wave fronts in a beam of light. The step, which lengthens or shortens according to the nature of the medium traversed, corresponds to the wave length of light; and the grass and ice, which offer more or less impediment to the column, correspond to transparent media of varying optical density. If we assume that the step of the marching man is shortened when he passes from grass to ice in the proportion of  $1\frac{1}{2} : 1$  we shall have a precise equivalent, so far as the mathematical theory is concerned, of a wedge of glass in an atmosphere of air. The diagram then illustrates what would happen to a beam of light transmitted through the field of an optical instrument if that field were occupied by a fragment of glass having the sectional formation shown by the diagram.

Herein lies the principle of which the microscopist takes advan-



FIG. 1.

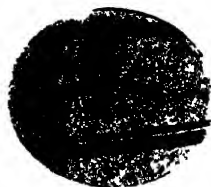


FIG. 2



FIG. 3.



FIG. 4



tage to produce dark outlines on a bright field or bright outlines on a dark field. Since neighbouring beams of light can thus be made to take different paths it is quite possible to arrange the eye-piece so that it may catch the one and miss the other beam; and, according as the one rejected comes from the margin of the object or from the background, so the image will be outlined dark or outlined bright, in either case in contrast with the field. The effects are known as bright field or dark field illumination, the case of dark field illumination being exactly analogous to the effect obtained by artists by means of cross lighting. The most universally familiar example of cross lighting is the gibbous or crescent moon, upon the surface of which the mountain tops and salient points stand out from a sea of shadow. Fig. 4 is a diatom shown under dark field illumination, the instrument being so arranged that the light from the field escapes the eye-piece, while the light refracted by the silex of the valve is transmitted to the eye-piece and furnishes the picture seen in the photograph. The reciprocal case of bright field illumination is illustrated by Fig. 2.

The application of this mode of producing a picture is evidently subject to this limitation, that light can be thrown upon the object under an angle so wide that some of it shall reach the eye-piece and some of it shall travel out of the instrument altogether. Hence it is difficult of application when objectives of very wide angle are used, and when the angle of the condenser which supplies the light is less than that of the objective which receives it the method of dark field illumination cannot be applied at all. This limitation has long been felt to be a considerable drawback in connection with the use of high power lenses and especially of immersion lenses, which always have great angular grasp. The problem thus presented, of devising a system of dark field illumination which shall be applicable to object glasses of the widest possible aperture, has recently been attacked, and with notable success, by Dr. Siedentopf, who has succeeded by its means in rendering visible objects so minute and clustered so close to one another that by no other known contrivance can they be rendered separately visible at all. Thus he has demonstrated—to take one example only—the minute particles of gold which, disseminated through a piece of glass, impart to it by their combined effect a ruby colour. Viewed under the highest magnifying power and under any ordinary illumination these massed particles of gold would appear at best as nothing more definite than a luminous haze. But by means of the Siedentopf apparatus the illuminating beam is thrown in at the side of the specimen and crosses the field of view at right angles to the axis of the instrument, so that if it were not for the reflection and refraction of the light at very wide angles to its original direction no single ray would find its way to the eye of the observer looking down the instrument. But even this would not suffice to bring individual particles of disseminated gold into view if any considerable thickness of the specimen were so lighted up, for

in that case the diffused light from illuminated particles lying above and below the focal plane would swamp the light emanating from the focal plane itself, and would substitute a luminous haze for a definite image, obscuring the focused picture precisely as a fog wraps and obscures the objects of a landscape. To provide against this difficulty Dr. Siedentopf employs a beam of light which, while broad enough to fill the entire field of the instrument, is very shallow in the direction of the line of sight. He takes as his source of light a narrow slit like the slit of a spectroscope, arranges it in a horizontal position, and illuminating this slit by an electric arc, he forms by means of a suitable and suitably mounted lens an image of the slit in the very middle of the field of the microscope. The beam so transmitted is, of course, extremely shallow at the focal point where it is a reduced image of the external slit. Thus the passage of the beam makes an optical section of the specimen so thin in the middle of the field that the gold particles included in it stand out as individual objects against the dark background of the unilluminated glass before and behind it in the line of sight. Under these conditions it is possible to exhibit particles, however small, provided only that they are sufficiently bright to be visible, and with a source of light so powerful as that which Dr. Siedentopf's apparatus enables us to employ that limit includes bodies which are extremely minute. The disseminated particles of gold in ruby glass, to take the example already cited, can thus be seen with such precision that their distances apart can be directly measured.\*

The particles of gold themselves, which appear as mere shining points, are so excessively small as to be beyond the imaging power of any microscope as yet constructed, but in aggregation they form a picture which is perfectly defined, so that it can be photographed or drawn and the space relations of its constituent parts accurately determined. In this, the latest development of the art of lighting the stage, we seem to have pressed the artifice of dark field illumination to the full limit of its theoretical capacity.

Passing now to the second of the topics with which we have to deal this evening, we are confronted by a question which may be formulated thus: Assuming that we have an object suitably mounted and suitably lighted on the stage of the microscope, how is the best representation of that object in the form of an image to be secured?

This question suggests at once the highly technical subject of lens correction and the structure of object glasses. That, however, is much too technical to be attempted on this occasion, but it is not possible to allude to it at the present time, even for the purpose of dismissing the subject, without recalling in this connection the name of the late Professor Abbe, whose untimely death a few

\* A specimen of Dr. Siedentopf's apparatus exhibiting the particles of gold in ruby glass was shown by the firm of Carl Zeiss, of Jena, in the Library of the Royal Institution at the close of the lecture.

weeks ago has deprived the world of the labours of one of the most successful makers of these appliances, and one from whose inventive powers applied to this subject matter much might still have been expected had his life been prolonged. But, while putting aside the more technical and intricate questions related to lens construction, which are and always will be connected with the name of Abbe, attention may be drawn, and perhaps usefully, to a proposition concerning the limit of useful magnifying power in the microscope objective, which was formulated and proved by Helmholtz so long ago as 1874, but has been strangely overlooked by writers on the subject since that date. According to that theorem, the object glass reaches the limit of its useful development in the direction of increased magnifying power so soon as, by reason of the shortening of its focal length, the diameter of the object glass in its principal plane is reduced to something not much less than the diameter of the pupil of the observer's eye. The reason of this may be shortly stated in this way: the human eye is not a homogeneous and perfectly transparent body like a well made lens of glass or crystal; on the contrary, its mass is intersected by connective tissue, and very commonly the aqueous humour is infested by minute opacities, while through the whole structure blood corpuscles circulate, carrying oxygen and minute shadows into every part. When the retinal picture is formed of broad beams of light, these small obstructions are unnoticed, the eye can look round them by means of the unobstructed rays which enter into the beam. But if the diameter of the beams which furnish the picture is cut down to something commensurable with the diameter of the obstruction, then the loss of light occasioned by it is serious, and may, when sufficiently pronounced, cause a visible shadow of the obstruction to be projected upon the picture. The same effect of intrusive shadows is produced by specks of dust and imperfections of polish in the ocular, and by the combined effect of all these causes a practical limit is put to the magnifying power which can be usefully employed. Object glasses can be made, and have been made, with as short focal length as  $\frac{1}{10}$  of an inch. But they are mere curiosities, possessing no practical advantage over the  $\frac{1}{8}$ ,  $\frac{1}{10}$  and  $\frac{1}{12}$  in common use. Added magnifying power to any required extent can be obtained by means of high-power oculars, and Helmholtz has shown that the image formed in that way may be just as perfect as the image formed by an object glass of higher magnifying power backed by a lower eye-piece. In fact, the one system is the exact optical equivalent of the other, and the object glass of greater focal length has the advantage of a greater working distance from its object. Thus, in practice, the high-power objective has come to have a diameter about equal to that of the pupil of the human eye, but this—although a theoretical reason for the rule was published thirty years ago, and by no less a writer than Helmholtz—has in fact been reached as the result of

practical experience, the empirical process of trial and error, rather than of scientific deduction, for the practical opticians have treated Helmholtz's investigation of the laws of the microscope with most singular neglect.

Before passing away from this branch of the subject, it will be interesting in this room to refer to certain experiments which at the present time are in a very different position, for they are as yet quite immature, and the special interest attaching to them arises from the circumstance that they have been suggested, and very recently, by certain theoretical conclusions deduced by Lord Rayleigh from the wave theory of light. It has been commonly assumed by earlier writers, and was assumed by Helmholtz in his discussion of the theory of the microscope, that the instrument would develop its utmost resolving power when the stage was so illuminated that each part of it should shine as nearly as possible with independent light. To make the meaning of this proposition clear, suppose that you fix your gaze upon a candle flame; it all appears to be of one colour and one brightness, but you know that the uniformity is rather apparent than real, and results from the averaging by the eye of an immense number of impulses received from every point upon the luminous surface, which impulses are individually by no means all alike, but range between wide limits of variation in colour and brightness. In a word, every point is, in respect of the light which it emits, independent of every other point, and this independence of its various parts, down to the minutest into which it can be subdivided, is characteristic of a self-luminous body. Next, in contrast with this, suppose that the light of the candle is received not directly from the flame itself, but indirectly by transmission through a sheet of ground glass, or by reflection from the surface of a sheet of white paper. In that case it is plain that adjacent points upon the luminous surface—the ground glass or the white paper, as the case might be—would not be independently illuminated. They would all shine at any moment with the same borrowed light derived equally from all parts of the candle flame. Therefore, as the same components at all times enter into the light transmitted from every part of the secondary source, it will follow that this secondary source will shine with a really uniform—i.e. very approximately uniform—illumination in all its parts.

The question now proposed may be formulated thus: It being open to the microscopist to choose such a form of illumination as may best suit the object with which he is dealing, let us suppose that the object is extremely minute, and that it is of first importance, therefore, for him to develop the full resolving power of his instrument: will this be best accomplished by lighting the stage of the instrument so that every part of it shall shine, as in a candle flame, with independent light, or, as in the case of the white paper, with light of more or less uniform phase?

Now it has hitherto been taken for granted that the highest resolving power would be developed by means of the self luminous surface; but quite recently Lord Rayleigh has made this assumption the subject of mathematical investigation,\* with the result that it now appears that certain forms of regular illumination—light structure, as it may, perhaps, be termed—afford a background on which very minute objects can be better displayed and more vigorously delineated than upon the structureless field of a self-luminous area. Lord Rayleigh's discussion of this topic has been purely mathematical, and he must not be held responsible for the attempts which have been made to carry into practice the suggestion contained in his paper. But such attempts have been made, and with a sufficient promise of success to warrant a brief reference to the matter in this place, although they are at present purely tentative, and indeed, in the initial stages of a tentative effort.

The exact practical problem, as it results from Lord Rayleigh's theoretical conclusions, is to illuminate the stage of the microscope with light, the phase of which shall change according to a rule of variation from point to point, so that where a strong defining line occurs in the object, it may be reinforced by the interference of the light given off by adjacent parts of the luminous field. Such a condition would not necessarily be satisfied by the borrowed light with which a sheet of white paper, or say, the surface of the moon, shines. But the method of mixing by reflection the emanations from a primary light source is by no means the only mode in which a regular structure can be given to a beam of light. Many other plans can be followed, and one which is particularly susceptible of nice adjustment and exact control is the employment for the illumination of the field of the diffraction fringe formed upon the edge of a shadow. It can be shown that in such a diffraction fringe the phase of the light varies from point to point according to a law which results in isophasal zones drawn parallel to the edge of the shadow; and experiment shows that when such zones are formed in the luminous field of a microscope, and are arranged parallel to the outlines of an object lying in that field, the outlines receive a notable accession of density. Thus, if a test plate, say, for example, a Nobert or Grayson ruling, be taken and viewed by means of an objective which is barely powerful enough to resolve it under full illumination, it may be seen strongly resolved if for the full light a suitably graduated diffraction fringe be substituted.

This experiment may be repeated upon a large scale by means of the very simple appliances which are here upon the table. The lantern is arranged so as to yield a slightly divergent beam of light. The central pencil of this divergent beam may be regarded as consisting of substantially parallel rays, like a beam of sunlight, and

\* See the Journal of the Royal Microscopical Society, 1903, p. 474.

this central pencil is used to throw upon the screen the magnified shadow—which can be seen from every part of this theatre—of a toilet comb. The coarser teeth throw separate and well-defined shadows, so that in this part of the picture the image is well resolved. But the fine teeth are too fine to yield a resolved picture, and in this part of the image, therefore, the structure is entirely lost. But now, if between the comb and the source of light I introduce the blade of a table knife, with its straight edge held parallel to the teeth of the comb, you will observe that the edge of the shadow thrown by the knife is blurred by a diffraction fringe, and that where this diffraction fringe serves as a background to the picture, the images of the coarse teeth become much stronger than before, and the fine teeth are represented by a fully resolved image. Exactly the same effect is produced in the microscope by the artifice of introducing such a diffraction fringe into the background of the picture which you want to exhibit with improved definition. Figs. 5 and 6 are photographs of the shadows exhibited in this experiment.\*

Assuming the best possible image to be formed of the object exhibited upon the stage, there still remains the problem of seeing the image so provided. To see an image is not quite the same thing as to see a material object, for the object can be seen from many points of view; the image, if it be an aerial image, will be visible only through a limited angle, and when the image is highly magnified as well as aerial, this limited angle is very limited indeed. Mere limitation of this angle of view is of no great consequence to the user of an optical instrument, so long as the beam emitted by the instrument is large enough to fill the pupil of the observer's eye. But Lagrange proved that, in the case of a telescope, the diameter of the emergent pencil is proportioned inversely to the magnifying power of the instrument and directly to the diameter of the object-glass. In 1874 Helmholtz extended Lagrange's theorem to the microscope, showing that in that instrument also the emergent pencil of light has a diameter inversely proportional to the magnifying power. But as the microscope cannot be fitted, like the telescope, with an object-glass many inches in diameter, it is not possible to expand the transmitted beam of light by the expedient of using a large object-glass. Helmholtz showed that in the case of a microscope it is the angle under which light from the object is received at the front face of the objective which determines the breadth of the transmitted beam, and he modified Lagrange's formula accordingly, so as to express the law that the emergent pencil of light is proportional directly to the "numerical aperture," or, as he called it, the normal magnifying power, and inversely to the actual magnifying power of the instrument.

\* In the photographs which have been prepared for the illustration of this paper, a thick wire has been substituted for the knife-blade, by which means two diffraction fringes (one at the upper, the other at the lower edge of the wire) are obtained in place of one.



FIG 5



FIG 6

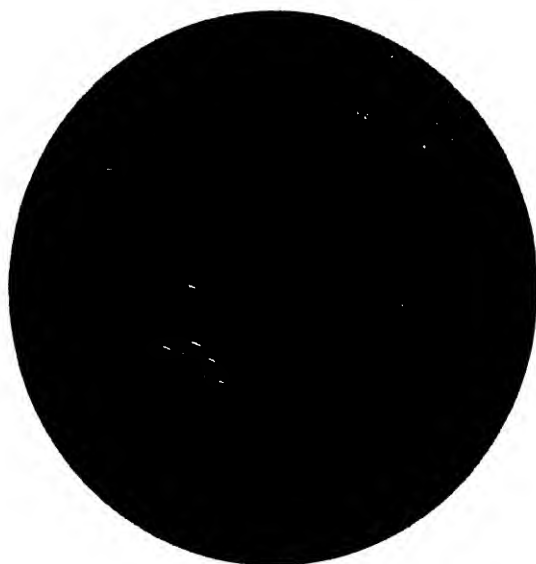


FIG. 7.

From this principle it follows that with very high magnifying powers the emergent pencil of light will become extremely small. Thus, in a microscope exhibiting to the eye a magnification of what is conventionally accounted 1000 diameters, the pencil of light which enters the eye has a diameter of about  $\frac{1}{100}$  inch. The actual magnifying power of an instrument reckoned at 1000 according to the opticians' convention is about 80. It will, therefore, be understood that if photographs having any considerable magnification are to be produced it must be by the use of extremely narrow beams of light.

Reference has been already made to the inconveniences which beset the employment of such very narrow beams of light. They are more serious even in visual microscopy than in photomicrography, for, although it is possible by careful polishing and scrupulous cleaning to purge a lens of dust and obstructions, it is not possible by any expedients so to clear the eye. Eyelashes, tears, and *muscae volitantes* at least will be introduced into the picture in addition to any specks which may be lodged on the ocular or on the back of the objective. Hence a limit is soon put to the enterprise of the instrument maker who essays to exhibit a really large scale image to the eye of his customer. Fig. 7 is a photograph of typhoid bacillus blemished in this way. The photograph does not, of course, exhibit eyelashes or specks seated in the eye. Blemishes of that sort would in practice be added to what is here shown, with the result of still further deteriorating the image. This particular specimen has been produced under extreme magnifying power, such indeed as is never used for direct vision, and is used only in connection with photography when special appliances are employed to avoid the use of an ocular. This, however, has been taken with an ordinary ocular and by means of a camera specially constructed to fill the exact position taken in the optical system of the microscope by an observer's eye. As it stands, the magnification is about 7000 diameters, the picture having been enlarged to a convenient scale for reproduction by photographic process. The original negative had a magnification of 1900 diameters, equivalent to about 6000 according to the opticians' convention, for the camera used has about one third of the magnifying power of the conventional human eye. It is not surprising that microscope makers have given up the attempt to produce pictures upon this scale of magnification, seeing that the enlargement of scale involves so much corruption of the image.

Down to the present time this defect of a highly magnified image has been thought to be manifestly insuperable. Even if the users of microscopes could be relied upon to take the extraordinary pains necessary to keep their lenses absolutely clean, they could not keep their eyes clean. Even to preserve the ocular against dust is no small matter. It might be supposed that the ocular which supplied the dust and minute hairs that so seriously impair Fig. 7 was selected



as an awful example of what an ocular may come to under exemplary neglect, but in fact there is nothing at all exceptional in its condition. At moderate magnifying powers these intrusive particles are quite invisible, and the ocular in fact was in the condition in which an ordinarily careful user would be accustomed to employ it. Nothing but the scale is out of the common, and with the high magnifying power employed the narrow beams which can be quenched by these diminutive obstructions are associated by a mathematical law. It was perfectly reasonable, therefore, for the instrument makers to regard the presentation to the eye of a satisfactory "super-amplified" image as an insoluble problem of physics.

But the insoluble problem has quite recently been solved, and by the simplest imaginable expedient. Everybody knows that when a magic lantern picture is thrown upon a screen it becomes just as visible as a real object, that is to say, the angle from which it can be viewed becomes so widely extended that the picture is visible to an entire audience when transmitted by a screen, although it would be visible only by the one or two beholders who could stand approximately in the axis of collimation, if the picture were aerial. The same expedient gets over all the difficulties of high power magnification in a microscope, and is employed in an instrument which you will be invited to examine in the library this evening. Fig. 8 is a diagram of this instrument. The arm which is extended from the tripod at its side into the tube of the microscope carries at its free extremity a small screen of finely ground glass. This glass screen is by it held in the image plane of the microscope, and receives the image formed by the object. Its grain scatters the light of this image over a wide angle, exactly as the magic lantern screen scatters the light of a lantern picture, so that the Lagrange relation between the angle of the beam and its magnifying power is broken down, and the screened image can now be seen, as if it were a real object, under any desired angle. Such an image may be subjected without impairment to high magnifying power, and so the eye-lens of the ocular is replaced by a compound microscope fitted with a half-inch objective and an ocular magnifying eight times. This system of "eye-piecing" yields, of course, an enormously super-amplified image, and it was with this apparatus, but minus the ground glass screen, that the photograph reproduced in Fig. 7 was taken. We shall now be able to see, by means of a strictly comparable photograph of the same object taken with the screen, what is the optical advantage accruing from its use.

One very obvious optical *disadvantage* there will clearly be unless steps are taken to avoid it, that is to say, the grain of the screen will itself be visible in the picture since it is displayed in the focal plane. Fig. 9 shows this result, and although the dust has disappeared, the grain of the roughened glass screen is itself a much worse blemish than any reasonable accumulation of dust and flymarks on the lenses

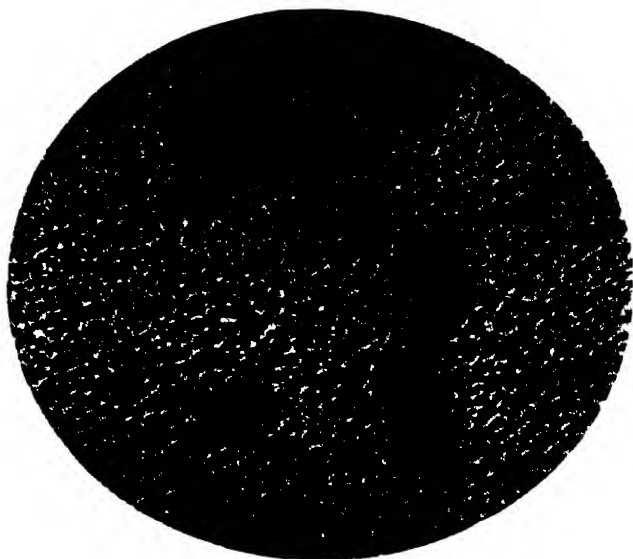


FIG. 9

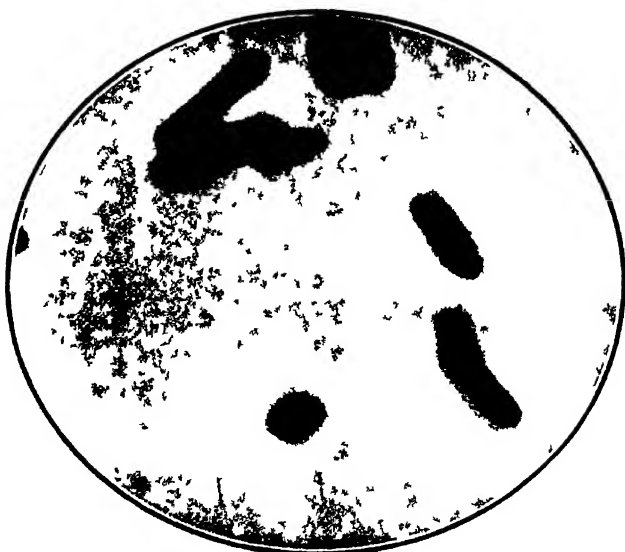


FIG. 11.

of the microscope. Microscopists call Fig. 7 a "rotten image." Fortunately they have not been called upon to find a description for

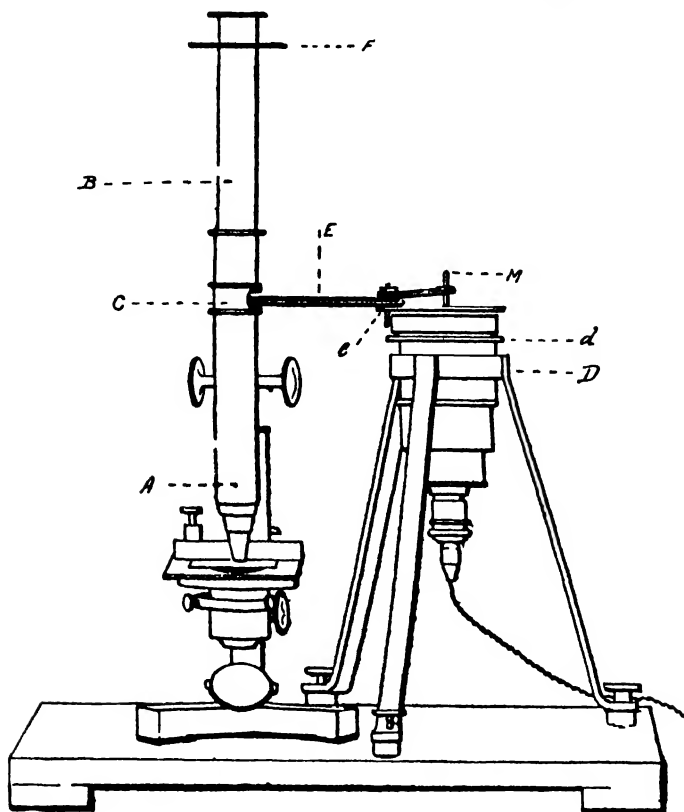


FIG. 8.

A is the principal microscope.

B is the auxiliary microscope which replaces the eye-piece of the principal instrument.

C is the image plane of the principal microscope, and indicates the position in which the oscillating screen is mounted.

D is the tripod supporting the screen and its motor.

*d* is a focusing ring by which the screen supporting arm is adjusted to the correct level.

E is the screen supporting arm, and *e* is its elbow joint.

F is a ring for coarse focusing of the auxiliary microscope.

M is an electric motor driving the oscillating screen.

Fig. 9, for the vice of that image, formidable as it looks, is very easily corrected. The grain of the glass is conspicuous only so long

as it is at rest. By keeping it in motion it can be rendered invisible, and the motion need not be rapid for, like the grain itself, the movement is magnified by the upper microscope through which it is viewed. But two precautions must be observed. The screen must be kept accurately in the focal plane and it must not move in a closed path. The first is obvious and it will appear upon a moment's reflection that if the bright points upon the screen described closed paths in the field of view those paths would be delineated in the picture by bright lines.

The contrivance is illustrated in Fig. 10 by which in this piece of apparatus the necessary oscillation in a path too complicated to be followed by the eye or traceable on a photographic plate is imparted to the screen. Here a pulley revolves upon a stud, the stud being perforated to allow the image-forming beam to pass. This foramen in the stud occupies in use the exact centre of the tube of the instrument. The top of the stud is flattened and forms a platform upon which the ground-glass screen rests. Upon the upper face of the pulley a ring is mounted eccentrically, and in the hollow of this circular ring the screen lies; fitting it very loosely. Now when the pulley rotates it will of course rotate the eccentric ring, and the ring, wobbling round, will drag the screen round with it in its eccentric revolution. But the screen, being loose within the ring and resting on the stationary stud, will tend to lag behind the ring in its movement and will roll upon its edge within the ring with a relatively backward motion. The whole result is that the screen oscillates and revolves about a constantly varying centre of motion, and the paths described by its various parts do not return into themselves.

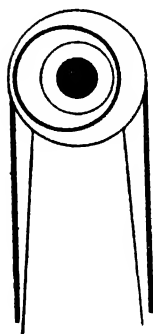


FIG. 10.

By this simple expedient the whole difficulty is overcome. The screen abolishes the intrusive images of the dust and foreign matter; the motion renders the screen itself invisible. Fig. 11 is a photograph of the image which with these precautions can be obtained even under such extreme conditions of super-amplification as those above described. And the image so formed is just as perfect when viewed directly as when recorded by the aid of photography.

[J. W. G.]

Friday, March 10, 1905.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR J. J. THOMSON, LL.D. D.Sc. F.R.S., Cavendish Professor  
of Experimental Physics, University of Cambridge.

*The Structure of the Atom.*

IN 1897 I had the pleasure of bringing before the Royal Institution experiments showing the existence of *corpuscles*, i. e. negatively electrified bodies having a mass exceedingly small compared with that of an atom of hydrogen, until then the smallest mass recognised in physics. A suggestive and striking property of these corpuscles is that they are always the same from whatever source they may be derived. The corpuscles were first detected in the rays which are projected from the cathode when an electric discharge passes through a vacuum tube, and it was found that whatever the nature of the residual gas in the tube, or whatever the metal used for the electrodes, the corpuscles were always the same. Other sources of corpuscles soon came to light; they were found to be projected from incandescent metals, from metals illuminated by ultra-violet light, and from radio-active substances; but whatever their source the corpuscles were always the same. This fact, in conjunction with their small mass, suggests that these corpuscles form a part of the atom, and my object this evening is to discuss the properties of an atom built up of corpuscles. As these corpuscles are all negatively electrified, they will repel each other, and so if an atom is a collection of corpuscles, there must in addition to the corpuscles be something to hold them together; if the corpuscles form the bricks of the structure, we require mortar to keep them together. I shall suppose that positive electricity acts as the mortar, and that the corpuscles are kept together by the attraction of the positive electricity. We do not know nearly so much about positive as we do about negative electricity; we have never obtained positive electricity associated with masses less than the mass of an atom; in fact, appearances all point to the conclusion that positive electrification is produced by the withdrawal of corpuscles from a previously neutral body. These conditions are satisfied, if we suppose with Lord Kelvin that in the atom we have a sphere uniformly filled with positive electricity, and that the corpuscles are immersed in this sphere. The attraction of the

positive electricity will tend to draw the corpuscles to the centre ; the mutual repulsion between the corpuscles will tend to drive them away, and they will arrange themselves so that these tendencies neutralise each other.

Let us now consider the kind of atom we could build up out of corpuscles and positive electricity. The mathematical investigation of this problem leads to the following results. The simplest atom containing 1 corpuscle would have 1 corpuscle at the centre of the sphere of positive electrification ; the 2 corpuscle atom would have the 2 corpuscles separated by a distance equal to the radius of this sphere ; the 3 corpuscle atom would have the 3 corpuscles at the points of an equilateral triangle, whose side is equal to the radius of the sphere ; 4 corpuscles would be at the corners of a regular tetra-

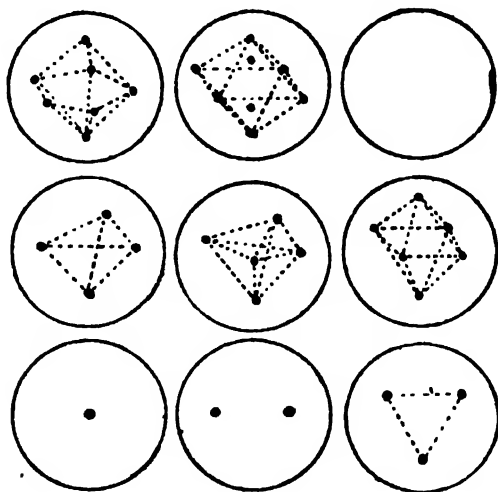


FIG. 1.

hedron, whose side is equal to the radius of the sphere ; 5 corpuscles are situated, 4 at the corners and 1 at the centre of a tetrahedron ; 6 at the corners of an octahedron ; 7 and 8 are more complicated, as the simplest arrangements for 7 and 8, an octahedron with 1 at the centre and a cube, are both unstable ; and for 7 we have a ring of 5 in one plane with 2 on a line through the centre at right angles to the plane ; and 8 we have the octahedron with 2 inside. These arrangements are shown in Fig. 1.

When the number of corpuscles is large, the calculation of the positions of equilibrium becomes very laborious, especially the determination of the stability of the various arrangements. I will therefore treat the subject from an experimental point of view, and apply to this purpose some experiments made with a different object many

years ago by an American physicist, Professor Mayer. The problem of the structure of the atom is to find how a number of bodies, which repel each other with forces inversely proportional to the square of the distance between them, will arrange themselves when under the attraction of a force which tends to drag them to a fixed point. In these experiments the corpuscles are replaced by magnetized needles pushed through cork discs and floating on water. These needles having their poles all pointing in the same way repel each other like the corpuscles; the attractive force is due to another magnet placed above the surface of the water, the lower pole of this magnet being of the opposite sign to the upper pole of the floating magnets. This magnet attracts the needles with a force directed to the point on the water surface vertically below the pole of the magnet. The forces acting on the needles are thus analogous to those acting on the corpuscles in 'our' model atom, with the limitation that the needles are constrained to move in one plane.

As I throw needle after needle into the water you see that they arrange themselves in definite patterns, 3 magnets at the corners of a triangle, 4 at the corners of a square, 5 at the corners of a pentagon; when, however, I throw in the sixth needle this sequence is broken. The 6 needles do not arrange themselves at the corners of a hexagon, but 5 go to the corners of a pentagon, and 1 goes to the middle; a ring of six with none in the inside is unstable. When, however, I throw in a seventh, you see I get the ring of 6 with 1 in the middle; thus a ring of 6, though unstable when hollow, becomes stable as soon as 1 is put in the inside. This is an illustration of the fundamental principle in the architecture of the atom: the structure must be substantial. If you have a certain display of corpuscles on the outside, you must have a corresponding supply in the interior; these atoms cannot have more than a certain proportion of their wares in their windows. If you have a good foundation, however, you can get a large number on the outside. Thus we saw that when the ring was hollow, 5 was the largest number of needles that could be stable. I place in the centre a large bunch of needles and you see that we get an outer ring containing 22 needles in stable equilibrium.

The proportion between the number which is in the outer ring and the number inside required to make the equilibrium stable is shown in the following table:

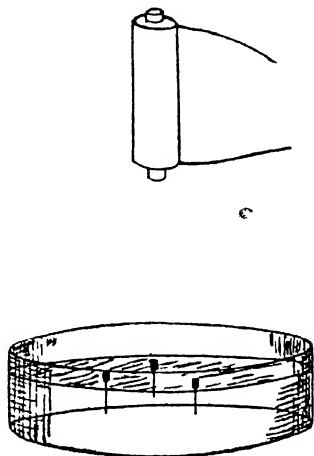


FIG. 2.

Number in outer ring	5	6	7	8	9	10	12	13	15	20	30	40
Number inside. . .	0	1	1	1	2	3	8	10	15	39	101	232

We see from these illustrations how the corpuscles would arrange themselves in the atom, confining ourselves for the present to the case where the corpuscles are constrained to move in one plane. The corpuscles will arrange themselves in a series of rings, the number of corpuscles in the rings getting greater and greater as the radius of the ring gets greater. By the aid of the above table we can readily calculate the way any number of corpuscles will arrange themselves. Let us suppose for example we have 20 corpuscles and try to arrange them so as to have as few rings as possible; we see from the table that we cannot have more than 12 in the outside ring, for 13 would require 10 inside, and would be impossible with less than 23 corpuscles: thus 12 will be the number in the outside ring and there are eight left to dispose of; these cannot form a single ring with no corpuscles inside, as 5 is the greatest number that can do this; the 8 corpuscles will therefore break up into two systems, a ring of 7 with 1 inside. You see that when I try the experiment with 20 magnets they arrange themselves in this way.

If we follow the kind of atoms produced as we gradually increase the number of corpuscles, we find that certain arrangements will recur again and again; thus take the case of 20 corpuscles; this consists of the arrangement 1-7-12, the arrangement for 8 is 1-7; the atom of 20 corpuscles may be regarded as formed by putting another storey to the atom of 8 corpuscles; if we go to 37 corpuscles, we find the arrangement is 1-7-12-17, i.e. another storey added to the atom of 20, while for 56 we have 1-7-12-17-19, the atom of 37 with another storey added. Thus the possible atoms formed by numbers of corpuscles from one to infinity could be arranged in classes, in which each member of the class is formed by adding another storey to the preceding member; the structures of all the atoms in this class have much in common, and we might therefore expect the physical as well as the chemical properties of the atoms to have a general resemblance to each other. This property is, I think, analogous to that indicated by the periodic law in chemistry. We know that if we arrange the elements in the order of their atomic weights, then, as we proceed in the direction of increasing atomic weight, we come across an element, say lithium, with a certain property; we go on and after passing many elements which do not resemble lithium, we come across another, sodium, having many qualities in common with lithium. Then as we go on, we lose these properties and come across them again when we arrive at potassium; exactly the kind of recurrence we should get with our model atoms, if we suppose the number of corpuscles in the atom to be determined by its atomic weight.

Let me give another instance of the way the properties of these



atoms resemble the properties of the chemical atom. I will take the electro-chemical property of the atom. Some atoms, such as those of lithium, sodium, potassium, have a strong tendency to be positively electrified, while others like chlorine, bromine, iodine, tend to be negatively electrified. Now the way our model atom gets positively electrified, is by losing a negatively electrified corpuscle; thus, those atoms in which the corpuscles are loosely held would tend to get positively electrified, while those whose corpuscles are very firmly held would not get positively electrified, and might be able to bear the disturbance due to another corpuscle placed outside without disintegration, and with this additional corpuscle they would be negatively charged. Now let us see how this property would vary from atom to atom. I will take a numerical case. Suppose we begin with 59 corpuscles; we should have by the table 20 on the outside, and 39 in the inside; but as 39 is the least number of corpuscles that can hold a ring of 20 in stable equilibrium, the equilibrium of this atom would have nothing to spare; it would be in rather a tottery condition, and a corpuscle would be easily detached, leaving the atom positively charged. Let us now go to the atom with 60 corpuscles; it would still have 20 on the outside, but it would have 40 on the inside, and be more stable than 59; it would not so easily lose a corpuscle; and would not thus be so electro-positive as 59; as we go on up to 67 we have still 20 on the outside but get more and more in the inside, the difficulty of getting a corpuscle out therefore increasing, and the atom getting more and more electro-negative. Let us see what happens when we get to 68; here we have 21 on the outside and 47 inside, but as 47 is the smallest number which can keep 21 in equilibrium, this equilibrium is shaky, and as in the case of 59 corpuscles the atom would be very electro-positive. Thus, as we increase the atomic weight, we get for a certain range, a continual diminution in the electro-positive character; this goes on until we get to 67, then there is a sudden jump from the electro-negative 67 to the electro-positive 68, followed again for a time by a continual decrease in electro-positive characteristics with increasing atomic weight. Compare this with the behaviour of the atoms of the chemical elements

Li	Bi	Bo	C	N	O	Fl
Na	Mg	Al	Si	P	S	Cl
K	—	—	—	—	—	—

The electro-positive character diminishes as we proceed from Li to Fl, then there is a sudden change from the electro-negative Fl to the electro-positive Na, then another diminution in the electro-positive character to Cl, and then another sudden change from Cl to K.

The model atoms we are considering are all built up of the same materials—positive electricity and corpuscles—hence the atoms of any one element would furnish the raw materials for the atoms of any other element, and a rearrangement of the positive electricity and corpuscles

would produce transmutation of the elements. Whether the atoms of our elements will tend to break up into the atoms of other elements will depend upon the relative stability of the atoms, and the stability of an atom will depend mainly upon its potential energy; if this is large, the atom will be liable to break up or change. I have calculated for atoms containing from 1 to 8 corpuscles the potential energy of the atom per corpuscle: i.e. the potential energy of the atom divided by the number of corpuscles in the atom, making the assumption that positive electricity behaves like an incompressible fluid, i.e. that its density is invariable. The result is represented graphically in Fig. 3; the vertical ordinates represent the potential energy per corpuscle, the horizontal abscissæ the number of corpuscles in the atom. You will notice that the curve is a wavy line with peaks and valleys; the atoms corresponding to the peaks would have greater potential energy than their neighbours, and would therefore tend to be unstable, while those in the valleys, having relatively little potential energy, would be stable.

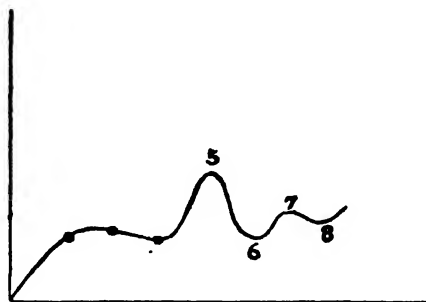


FIG. 3.

The case is in many respects very analogous to the case of a number of stones scattered over a hilly country whose section is represented by Fig. 3; the stones, if subject to disturbances, would run from the hills into the valleys, and though the stones might be uniformly distributed to begin with, yet in course of time they would accumulate in the valleys. So also in the chemical problem, though the number of atoms of the different elements might initially not be very unequal, yet, in course of time, those in the valleys would increase, and those on the peaks diminish, so that some elements would increase, while others would tend to become extinct. The smallest potential energy is that of an atom consisting of a single corpuscle; this is the goal which all the atoms would ultimately reach, if subject to disturbances sufficiently intense to lift them over the intervening peaks. Thus, on this view, the general trend of the universe would be towards simplification of the atom—though there might be local eddies. The final stage would be that in which all the atoms contained only one corpuscle. This result depends upon the assumption that the positive

electricity is incompressible, i.e. that its density is constant; if we had assumed that the volume of the positive electrification is the same whatever may be the quantity of electricity, we should have found that, although there would still have been changes from one element to another, the general trend would have been in the opposite direction, i.e. the simple atoms containing only one corpuscle would gradually condense into more and more complex atoms.

*Chemical Combination. Action of the Atoms on each other.*—We have hitherto confined our attention to the consideration of the stability of the arrangements of the corpuscles in the atom. We shall now proceed to discuss the question of the action of one atom on another, and the possibility of the existence of stable configurations of several atoms, in fact the problem of chemical combination.

As far as I know, the only cases in which the conditions for equilibrium or stable steady motion of several bodies acting upon each other have been investigated, is that suggested by the solar system; the case in which a number of bodies—suns, planets, satellites—attract each other with forces inversely proportional to the square of the distance between them. The complete solution of this problem, or anything approaching a complete solution, has proved to be beyond the powers of our mathematical analysis; but enough has been done to show that with this law of force, stable arrangements of the mutually attracting bodies only occur under stringent conditions. Thus, to take a very simple case, that of three bodies, it has been shown that, when the bodies are equal, there is no arrangement in which the steady motion is stable; if, however, the masses are very unequal, then it is possible for such an arrangement to exist. Another very interesting case is one investigated by Maxwell in connection with the theory of Saturn's rings. It is that of a large planet surrounded by a ring of satellites, each satellite following its neighbour at equal intervals round one circular orbit. Maxwell showed that this system was only stable under certain conditions, the most important being that the mass of the planet must be much greater than that of the satellite. The proportion between the mass of the smallest planet able to retain the ring in steady motion and the mass of one of the satellites increases very rapidly as the number of the satellites increases: if  $P$  is the mass of the planet,  $S$  that of a satellite,  $n$  the number of satellites, Maxwell showed  $P$  must be greater than  $\cdot 43 n^3 S$ . The consequences of this are interesting from the analogy shown in the case of chemical combination. Thus, suppose the mass of a satellite were  $\frac{1}{100}$  part of that of the planet, then the result shows that the planet could retain 1, 2, 3, 4, 5, 6 satellites, but not more than 6. With 6 satellites the planet is, to use a chemical term, saturated with satellites, and the behaviour of the system is equivalent to that of the atom of a sexavalent element, which can unite with 6 but with not more than 6 atoms of hydrogen.

The existence of a limit to the number of systems in a ring, which a central system can hold in stable equilibrium, is not peculiar to any

special law of force. We have already seen examples of it inside the atom, where the central force on the satellites is supposed to be proportional to the distance. We have just seen that it holds in the planetary system, where the central force varies inversely as the square of the distance. I have found that this limit exists for all the laws of force I have tried, although of course the number of satellites which can be held in equilibrium depends on, among other things, the law of force.

The law of the inverse square is not favourable to the formation of stable systems, even when, as in the astronomical problem, the forces between the various bodies are all attractive; it is quite inconsistent with stability when, as in the case of the chemical atoms, some of these bodies carry charges of the same sign, and so repel each other. Thus, suppose we have the central body charged with positive electricity, while the satellites are all negatively electrified, so that the central body attracts the satellites, while the satellites repel each other. With forces varying inversely as the square of the distances between them, it is easy to show that with more than one satellite stability is impossible.

The mathematical investigation of the case where the satellites repel each other shows that, in order to ensure stability, the central attraction must, in the neighbourhood of the satellite, increase when the distance of the satellite from the planet increases. Inside the atom we have supposed that the central attraction was proportional to the distance from the centre, so that in this region the central force increases rapidly with the distance at all points. It is not necessary for equilibrium that the increase should be as rapid as this, nor indeed that the force should everywhere increase with the distance; all that is necessary is that in the neighbourhood of the satellite the force should increase and not decrease as the distance increases.

It might appear at the outset as though atoms of the kind we have been considering, made up of positive electricity and corpuscles, could never form stable arrangements, for there is a theorem known as Earnshaw's theorem, to the effect that a system of bodies attracting or repelling each other with forces varying inversely as the square of the distance between them, cannot be in stable equilibrium. This result does not prevent the existence of stable arrangement of atoms in the molecule, for Earnshaw's theorem only applies to the case when the bodies are at rest; it does not preclude the existence of a state of steady motion, in which there is no relative motion of the atoms. Again, in the case of our atoms there are other forces besides the electrostatic attractions and repulsions, for if the corpuscles are in rotation inside the atom, they will produce magnetic forces, so that outside the atom, there will be a magnetic, as well as an electric field. The magnetic field will greatly promote the stability of the atoms if these are charged, for it will, if strong, practically prevent motion at right angles to the direction of the magnetic force, so that the arrangement of atoms will be stable provided the electrostatic

forces give stability for displacements *along* the lines of magnetic force. For example, if at any point near an atom the magnetic force were radial, then a second charged atom at this point would be in stable equilibrium, provided the radial attraction between the atoms at that point increased as the distance between the atoms increased.

Let us now consider the forces produced by an atom of the kind we have described. Take the case of an uncharged atom, i.e. one where the sum of the charges on the negatively electrified corpuscles is just equal to the positive charge in the sphere in which the corpuscles are supposed to be placed. Let us consider the radial force to the centre due to such an atom. Since there is as much positive as negative electricity in the atom, the average radial force taken over the surface of a sphere with its centre at the atom is zero; this does not mean that the radial force is everywhere zero, but that at some places it is directed towards the centre, and at others away from it. There

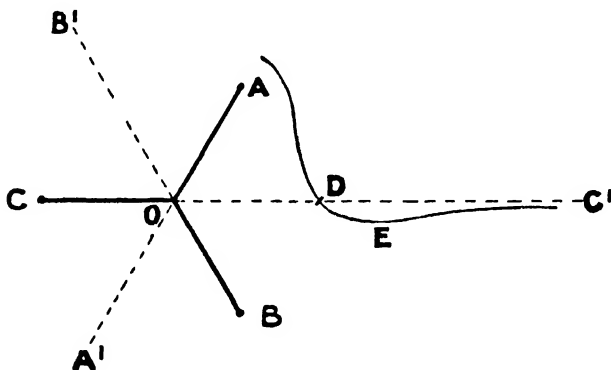


FIG. 4.

may be, as we shall see, certain directions in which the force changes from attraction to repulsion, or *vice-versâ*, as we travel outwards from the sphere.

Thus take the case of three corpuscles placed in a sphere. The corpuscles, when in equilibrium, are at the corners of an equilateral triangle  $ABC$ ; let  $O$  be the centre of the atoms of which these corpuscles form a part. Consider the force on a positively charged particle. As we travel from  $A$  radially outwards, we find that the force is always towards  $O$ , and gets smaller and smaller as we get further and further away. As the attraction diminishes as the distance increases, there is no place at which the particle would be in equilibrium, stable or unstable. Suppose, however, we travel outwards along  $OC$ , the prolongation of  $CO$ , then when the particle is just outside  $AB$ , the force on the particle is repulsive. This repulsive force diminishes as we recede from the atom and vanishes at a certain distance  $D$ ; at

greater distances from the atom than  $D$ , the force is attractive and remains attractive at all greater distances; thus a positively charged particle would be in equilibrium at  $D$ , and it is easy to see that the equilibrium would be stable, for if the particle were made to approach  $O$ , the repulsive force would drive it back to  $D$ , while, if the particle were to recede from  $D$ , the attractive force would drag it back. If we represent the relation between the radial force and the distance by a graph, a point above the horizontal axis corresponding to repulsion, and one below it to attraction, we obtain a curve of the following character. The curve crosses the axis at the point  $D$ , the place where the force vanishes; after passing  $D$ , the force which is now attractive increases as the distance from the atom increases, until a point  $E$  is reached when the force is a maximum; beyond  $E$  the attraction diminishes as the distance increases. Thus, since in the region  $DE$ , the force is attractive and increases as the distance increases, a positive particle, placed in this region, might be in stable equilibrium, while outside this region the equilibrium would be unstable.

There would, of course, by symmetry be similar regions on  $OA^1$ ,  $OB^1$ , the prolongations of  $OA$  and  $OB$  respectively. It will be seen



FIG. 5.

that the nature of the force between the atom and the charged particle, is of the type postulated by Boscovich, i.e. a repulsion at short distances succeeded by an attraction at greater ones. With the very simple type of atom we have been discussing, there is only one change from repulsion to attraction; with atoms containing more corpuscles, the graph representing the relation between force and distance becomes more complicated, and we may have several alternations between repulsion and attraction instead of only one as in Fig. 5.

However complicated the atom, a distribution of forces of this kind will only occur in a limited number of directions, or rather only along directions making small angles with a limited number of axes drawn in definite directions.

I have here an arrangement to show the change in direction of the force due to an atom. The atom is supposed to be one with three corpuscles; these are represented by the negative ends of three electromagnets arranged radially on a board, the positive ends of the magnets which represent the positive electrification in the sphere being at the centre. We see that along the lines  $OA^1$ ,  $OB^1$ ,  $OC^1$ , the magnetic force on a positive pole changes from repulsion to attraction at a

certain distance, and that the system can hold three floating magnets in stable equilibrium at a finite distance from its centre.

An atom analogous to the one we have just been considering would have the power of keeping three positively electrified particles

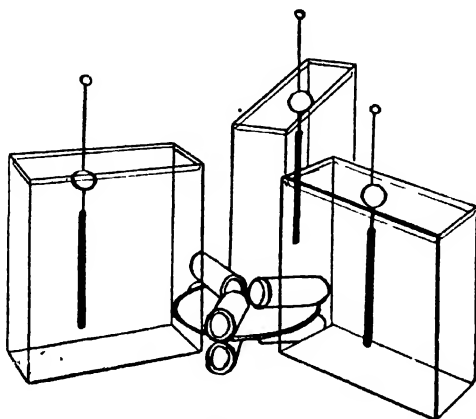


FIG. 6.

in stable equilibrium, provided these are placed at suitable distances along the lines  $OA^1$ ,  $OB^1$ ,  $OC^1$ . With other arrangements of corpuscles, we should get atoms able to keep negatively electrified particles in equilibrium. Thus, for example, if we have 5 corpuscles placed at the corners of a double pyramid as in Fig. 7, then along the lines  $OA$ ,  $OB$ ,  $OC$ , at suitable distances from  $O$  negatively electrified particles could be in equilibrium, even if the atom were uncharged. If, however, the central atom were uncharged while the satellites were charged, the molecule, as a whole, would be charged, whereas we know the molecule is electrically neutral; we must consider, therefore, what would be the effect of giving a charge of electricity to the central atom.

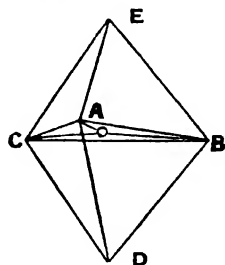


FIG. 7.

In the case of the three corpuscles, if we gave a negative charge to the central atom, the axes  $OA^1$ ,  $OB^1$ ,  $OC^1$ , might or might not cease to be axes of stable equilibrium for positively electrified particles. The effect of the charge would be to bring the point  $D$  of equilibrium closer to the atom—how much closer would depend upon the charge given to the atom; but as long as  $D$  kept outside the atom, stable equilibrium for positively electrified particles would

be possible ; if, however, D came inside the atom, the axes  $OA^1$ ,  $OB^1$ ,  $OC^1$ , would cease to be axes of possible equilibrium.

In some cases, the communication of a charge to the atom might, in addition to affecting the position of equilibrium along the axes for the uncharged atom, introduce axes of stability which did not exist when the atom was uncharged ; thus, in the case of a double pyramid Fig. 7, if we gave a positive charge to the atom, the axes  $OE$ ,  $OD$ , which were not axes of equilibrium for the uncharged atom, would become so for the charged one ; for if the atom had a positive charge, the force on the negatively electrified particle would at a point a great distance from the centre along  $OE$  be an attraction, while close to  $E$  it would be a repulsion ; there must be some point then when the force changes from repulsion to attraction, so that this axis will be one of equilibrium.

In the case of a more complicated atom giving a distribution of force changing from repulsion to attraction more than once, as in the case represented in Fig. 5, there would be places along this axis where a negatively electrified particle would be in stable equilibrium and other places where a positively electrified particle would be in stable equilibrium. The effect of giving a positive charge to this alone would be to make the positions of equilibrium for the negative particles approach the atom, those for positive particles recede from it ; the effect of a negative charge would displace those positions in the opposite directions.

The forces we have been considering are those exerted by an atom on a charged particle ; they would be a part (and in many cases, I think, the most important part) of the forces acting on a second atom, if that atom had an excess of one kind of electricity over the other. Remembering, however, that there is an electric field round an atom, even when it is uncharged, and that an uncharged atom is not an atom in which there is no electricity, but one where the negative charge is equal to the positive, we easily see that two uncharged atoms may exert forces on each other ; the calculation of these forces is, on account of the complex nature of the atom, very intricate, and I shall not go into it this evening. I shall treat the subject from the experimental side. I have here two systems, each built up of magnets, each containing as many positive as negative poles, and thus analogous to an uncharged atom ; one of them is suspended from the arm of a balance, Fig. 8. You see that I can place these systems so that they repel each other when close together and attract each other when further apart, so that these atoms would be in stable equilibrium under each other's influence when separated by the distance at which repulsion changes to attraction.

The force which an atom A exerts on another atom B may be conveniently divided into two parts : the first part, which we shall call the force of the E type, depends upon the charge on B ; it is proportional to this charge and independent of the structure of B, and we might, without altering this force, replace B by any atom we pleased,



provided it carried the same charge. The other part of the force, which we shall call the M part, is independent of the charge on B, but depends essentially on its structure; this part of the force would be entirely altered, if we replaced B by an atom of a different kind.

The question now arises, What part do these two types of force play in determining the nature of the molecule? Is the stability determined by forces of the E or of the M type?

The E forces depend on the charges carried by the atom, so that in those compounds in which stability is due to the E forces, the

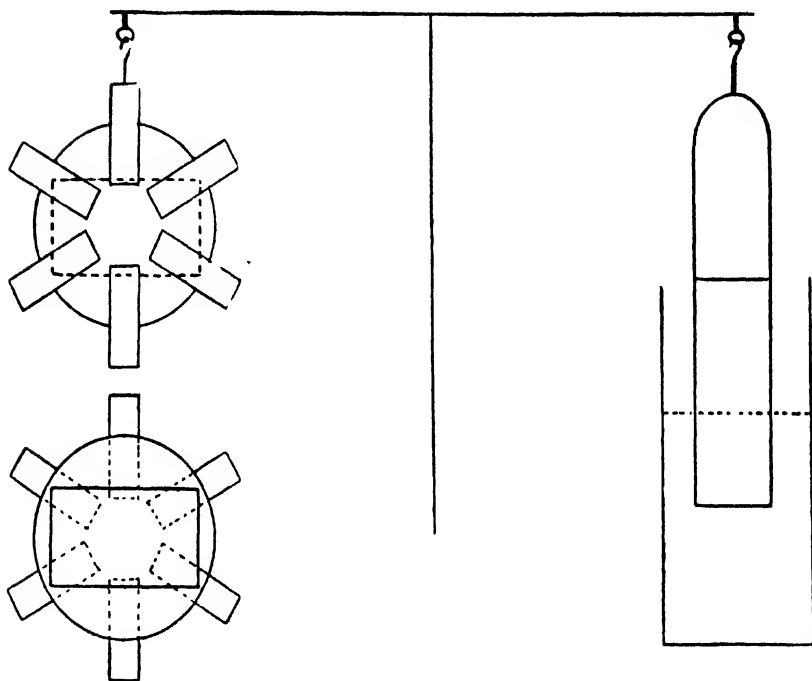


FIG. 8.

atoms must be charged. We are thus confronted with the question, Are the atoms in a molecule charged with electricity, or are they electrically neutral? Thus, to take a definite case, in the molecule of marsh gas, which we picture as a carbon atom at the centre of a tetrahedron with the four hydrogen atoms at the corners, are the hydrogen atoms charged with equal quantities of negative electricity, the carbon atom having a four-fold charge of positive, or are both carbon and hydrogen atoms uncharged? It is difficult to get direct evidence on this point, since the molecule as a whole is neutral on either supposi-

tion. There is, however, considerable indirect evidence to support the view that the atoms in many compounds are electrified. I may mention, as examples of such evidence, the power possessed by certain molecules, such as those of sugar, of rotating the plane of polarisation of light passing through them. This power, which is associated with the presence of the asymmetric carbon atom with four dissimilar atoms attached to it, is readily explained by the electromagnetic theory of light; if the atoms in the molecule are charged, it is difficult to see how uncharged atoms could produce sufficient rotation.

Let us consider the difference in the chemical properties of a substance according as the atoms in the molecules are held together by forces of the E or M type and one held together by the M type. Let us take the molecule of marsh gas as an example, and suppose that the molecule is in equilibrium under the E forces exerted by the carbon atom on the negatively electrified hydrogen atoms and the mutual repulsions between these atoms. The forces exerted by these hydrogen atoms depend entirely on the charge carried by the hydrogen atom; none of these forces would be affected if we replaced any or all of the hydrogen atoms by any atom which carried the same charge. Hence, without altering the architecture of the molecule, we might replace any or all of the hydrogen atoms by atoms of any univalent substance. In this case, the replacement of an atom by another of the same valency would be a very simple thing.

Suppose, however, that the atoms in the molecule were held together by forces of the M type, then the forces between two atoms would depend on the structure of both the atoms. If now we were to replace one of the H atoms by an atom of another kind, not only would the force exerted by the carbon atom on this atom be altered, but the forces exerted by the atoms on the remaining three hydrogen atoms would be radically changed; this change in the forces would involve a complete change in the structure of the molecule. Thus the effects of replacement are much more serious when the forces are of the M type than when they are of the E type. The forces of the E type are, I think, those which are most effective in binding atoms of different kinds together, while the M type of forces finds its chief scope in binding similar atoms together as in the molecule of an element, or as in the connecting the carbon atoms in the carbon compounds.

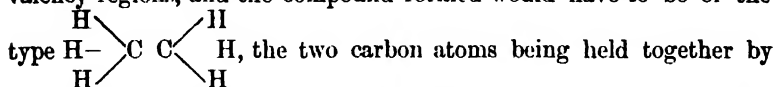
Let us sum up the results we have arrived at. We have seen that an atom built up of corpuscles in the way we have described possesses, whether charged or uncharged, the following properties. There are certain directions fixed in the atoms, along which or in directions not too remote from which, electrified particles, positively electrified for some kinds of atoms, negatively electrified for others, and either positively or negatively electrified for still other kinds of atoms, will be in stable equilibrium, if placed at suitable distances from the centre of the atom. We may call those directions the valency directions, and the regions within which the equilibrium is stable the valency regions. Those who are familiar with the beautiful theory of Van't Hoff and

Le Bel on the asymmetric carbon atom, which supposes that the attractions exerted by a carbon atom are exerted in certain definite directions, these directions being such that, if the carbon atom is at the centre of a regular tetrahedron, the attractions are along the lines drawn from the centre to the corners, will perceive the resemblance between that theory and the results we have been discussing. There is, however, an important difference between the two, for on our theory the forces exerted by the atom are not confined to any special direction; the atom exerts forces all round. It is only, however, in certain directions that these forces can keep a second atom in stable equilibrium. We picture, then, the atom A as being connected with a limited number of closed regions of finite size, and any body attached to the atom must be situated in one of these regions; when each of these regions is occupied by another atom, the atom A can hold no more bound to it, and is said to be saturated.

I have not time this evening to discuss in any detail further developments of these ideas. I may however, in conclusion, call attention to a point which is illustrated by the behaviour of the carbon compounds. Suppose that  $C_1 C_2$  are two carbon atoms near together. Then when



both atoms are present, regions  $\alpha, \beta$  near the line joining  $C_1 C_2$ , which were valency regions for  $C_1$  and  $C_2$  when these atoms were alone, may cease to be valency regions when both are present. For take the case when the stability is due to the magnetic force produced by the rotation of the corpuscles within the atoms. Along the line  $C_1 C_2$ , the magnetic force due to  $C_1$  and  $C_2$  will be in opposite directions, and in the region near the middle of  $C_1 C_2$  the resultant magnetic force would be very small, so that in this the equilibrium of a charged body would be unstable; thus  $\alpha \beta$  would cease to be valency regions. This reasoning would not apply to the valency regions of  $C_1$  on the side opposite to  $C_2$ , nor of those of  $C_2$  on the side away from  $C_1$ , so that six valency regions would remain. Thus if we consider the tetrahedra formed by the valency regions round our carbon atoms, then if two carbon atoms are placed so that two vertices of these tetrahedra come together, the regions near these vertices will cease to be valency regions, and the compound formed would have to be of the



forces of the M type. If the tetrahedra were placed so that two edges of the tetrahedra came together, we could show similarly that the four valency regions at the ends of the edge would be suppressed and the compound would be of the type,  $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ \text{H}-\text{C} & & \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ , while if two faces of the tetrahedra came together the valency regions in these faces would be suppressed, and the compound would be of the type  $\text{H}-\text{C}-\text{C}-\text{H}$ .

Friday, May 12, 1905.

THE EARL OF ROSSE, K.P. D.C.L. LL.D. D.Sc. F.R.S., Vice-President, in the Chair.

PROFESSOR ERNEST FOX NICHOLS.

Columbia University, New York.

*The Pressure due to Radiation.*

[ABSTRACT.]

THE first speculations upon a possible pressure due to radiation were suggested by the behaviour of comet tails.

Early in the sixteenth century, Pierre Apian announced that the tails of comets were always directed away from the sun, and a century later Kepler maintained that this repulsion was due to the pressure of sunlight. On the corpuscular theory of light it seemed plausible that the finely divided and very attenuated matter supposed to constitute comet tails, might experience a repulsion of which ordinary bodies gave no evidence.

The three intervening centuries from Kepler's time to our own, exhibit a long and very interesting record of conflicting opinions, and the account of many curious and inconclusive experiments.

In 1900-1901 the first experiments giving undoubted evidence of the existence of a pressure due to radiation were announced independently from Moscow by Professor Lebedew, and from New Hampshire by Nichols and Hull.

Maxwell had earlier maintained that radiation pressure was a necessary consequence of the Faraday-Maxwell electromagnetic theory of light, and after him, Bartoli was convinced that the same result should follow from the laws of thermodynamics. In computing the ratio of the pressure to the intensity of the radiation producing it, Maxwell and Bartoli were in exact agreement.

In the experiments of Nichols and Hull in which both the pressure and the intensity of a beam of light were measured, the ratio was found to agree with the Maxwell-Bartoli theory to within one part in a hundred. As the limit of accuracy of the observations was of this same order, the experimental verifications of the Maxwell-Bartoli theory may be accepted as complete.

Nichols's and Hull's experiments were described by the lecture

and the pressure exerted by a concentrated beam from an arc electric lamp on one vane of a delicately suspended torsion balance, was shown to the audience; and likewise the character of the disturbing action due to the gases present in the balance chamber.

Lebedew and Nichols and Hull succeeded in detecting radiation pressure, only because they were the first to systematically eliminate the disturbing forces due to the residual gases. Thus the cause of failure of the well directed efforts of earlier observers to isolate radiation pressure from the relatively powerful and uncertain gas forces exemplified in the Crookes radiometer was made clear.

A vacuum tube built by Nichols and Hull to illustrate the repulsion of comet tails by the sun was also shown. The form of the tube was that of an hour-glass. A very fine dust, prepared by calcining puff-ball spores, was mixed with the sand, and the pressure of a very powerful beam of light directed horizontally against the stream, just below the neck, drove the finer dust particles backward, while the heavier sand grains fell vertically.

The verification of the radiation pressure theory affords a means of extending our knowledge of many celestial phenomena and of broadening our theories concerning them. In the first place, the hitherto mysterious behaviour of comet tails is satisfactorily explained. The Newtonian gravitation theory is seen no longer to express the whole mutual action between bodies, for if either or both of the bodies be at a temperature above that of their surroundings, a correction must be added to include the radiation pressure between them. If the bodies are massive, and not too hot, the correction is insignificant; but Professor Poynting has shown that for two spherical black bodies of unit density 8 inches in diameter, if at a temperature of 30° Centigrade, the radiation pressure would just balance gravitational attraction, and the bodies would be entirely indifferent to each other, however near or far apart they might be.

A law of action between two bodies, alone in space, which takes account of both gravitation and radiation pressure is—

$$F = - \frac{\pi^2 a^2 b^2}{r^2} \left( \gamma \frac{\rho_1 \rho_2 a b}{16} - \sigma (T_1^4 + T_2^4) \right)$$

in which  $F$  is the force between two spheres of radii,  $a$  and  $b$ , of densities  $\rho_1$  and  $\rho_2$ ,  $r$  units distance apart, and at temperatures  $T_1$  and  $T_2$  absolute;  $\gamma$  is the gravitation constant, and  $\sigma$  is four times the radiation pressure between two spheres of unit radius and at two units distance apart when  $T_1 = 0^\circ$  and  $T_2 = 1^\circ$ , or the reverse.

Hereafter, therefore, in dealing with flocks of small stones or meteorites in space, and in computing the forces of condensation in a heated nebula, radiation pressure must be taken into the account.

Furthermore, radiation pressure is reciprocal. As a body which stops radiation feels a pressure, so also a body which is sending out

radiation in a given direction receives a backward pressure from its own emission. Professor Poynting has shown that when a hot body radiating equally in all directions is in motion, the intensity of its radiation will, in accordance with Döppler's principle, be slightly greater in front than behind ; hence the radiation pressures fore and aft will no longer balance, and there will be a resultant pressure tending to retard the body's motion.

If such a body should retain its temperature long enough it must inevitably come to rest, and not keep moving on for ever as we have previously believed.

[E. F. N.]

Friday, May 26, 1905.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR JULIUS WILHELM BRÜHL, Ph.D. Sc.D. *Hon. Mem. R.I.*,  
Professor in the University of Heidelberg.

*The Development of Spectro-Chemistry.*

ASSOCIATED as I am with Great Britain in my capacity as a Member of the Royal Institution, it is a special pleasure to me this evening to sketch to you the development of a branch of scientific study, the early history of which was enacted in this country—a country to which for many years I have been bound by close ties of sympathy. Many of you know already, and the others will see this evening, that I am in especial measure indebted to the science of this country for stimulus and encouragement in my own studies. It is a source of deep satisfaction to me to testify here to the gratitude which I owe to British science.

I.

§ 1. Last August it was my privilege to attend the Meeting of the British Association on the classic ground of Cambridge, and one sunny afternoon I found my way into that peculiarly effective example of collegiate architecture, the Chapel of Trinity College. The organ was playing Bach's Passacaglia, and I sat down quietly at the foot of the marble statue which bears the inscription :

NEWTON.

*Qui genus humanum ingenio superavit.*

The empty chapel was filled with harmony and with memories of the great man who once had sojourned there. And my thoughts wandered back to the past.

In 1666, almost two-and-a-half centuries ago, Isaac Newton, then a young bachelor, had decomposed a beam of sunshine, discovered the diverse refrangibility of the coloured rays, and explained the phenomena of dispersion.

The founder of scientific optics was also the first to perceive a connexion between differences in the composition of various natural bodies and their power of transmitting light.

Newton observed that oils, amber, sulphur, and other combustible bodies possess great refractive power, and he made the remarkable

statement that the diamond must also be combustible, because it refracts light so powerfully. This statement is indeed remarkable when we remember that in those distant times no one had any idea of the chemical composition of the diamond, or any conception of the nature of combustion.

But centuries of patient work were needed in order to recognise clearly the connexion between the chemical composition of different bodies and their power of refracting and dispersing light in different ways, i.e. of producing differently constituted spectra. To account for this connexion has become the task of "Spectro-Chemistry."

§ 2. Newton was also the first to fix a standard for measuring the refractive power of bodies. Starting from the emanation theory of light which he had himself founded, he diminished the square of the refractive index,  $n$ , by unity and regarded

$$n^2 - 1$$

as the expression for the refractive power. This power, reduced to constant density, i.e. divided by the specific gravity  $d$  of the body :

$$\frac{n^2 - 1}{d}$$

was called by Newton the "absolute refractive power."

§ 3. It was fully a hundred years later that Laplace, in his celebrated "*Mécanique céleste*," laid down the principle that the expression for refraction, derived from Newton's emanation-theory, must *for one and the same substance* be unaffected by changes in density caused by temperature and pressure—unaffected, that is, by the accidental density of a substance.

§ 4. The hitherto purely hypothetical formula for refraction acquired further scientific importance from the researches of Biot and Arago (1806), and Dulong (1826), on the refractive powers of gases and vapours. These, the first quantitative measurements of refractivity, seemed actually to confirm the theory that Newton's formula denotes a constant quantity which always remains unaffected by the accidents of temperature and pressure.

But with the triumph of the modern wave-theory of light, Newton's expression for refraction,  $\frac{n^2 - 1}{d}$ , lost its theoretical importance. New experiments soon showed that even its supposed independence of temperature and pressure did not in fact exist.

## II.

§ 5. In 1858, John Hall Gladstone, who was for some time Professor in this Institution, began his splendid series of optical researches, which he pursued with great success for over forty years. At first in collaboration with the Rev. T. Pelham Dale he investigated the dependence of refractivity on temperature in the case of



*fluid* substances. The important fact was at once established that Newton's expression for refraction,  $\frac{n^2 - 1}{d}$ , is not constant, but varies considerably with the temperature. On the other hand, it was found that the more simple ratio

$$\frac{n - 1}{d}$$

remains practically constant.

Now this ratio, just like the Newtonian constant confirmed by Biot and Arago, and by Dulong, applies also to gases and vapours. As, in the case of gases, the refractive index is very little different from unity, the numerical value of  $\frac{n^2 - 1}{d}$  is almost exactly twice that of  $\frac{n - 1}{d}$ .

### III.

§ 6. Soon after 1860, Hans Landolt came forward 'with his optical researches. He began by confirming the results of Gladstone and Dale. He proceeded a step further, however, by following the example of Biot and Arago, and comparing the refractivity not of equal, but of molecular quantities of the substances. If  $P$  represents the molecular weight, the product  $\left(\frac{n - 1}{d}\right) P$  is the *molecular refraction*.

§ 7. Landolt examined particularly the fundamental question whether a different grouping of the same number of atoms of the same elements—which is the cause of isomerism—has any influence on the optical properties of bodies.

He established the important fact that only the relative weight of the elements is of influence on the molecular refraction of a compound, while the different grouping of the atoms has no appreciable effect; and this made it possible to determine the atomic refractions of the elements. The atomic refraction of carbon, for instance, was obtained by comparing the molecular refractions of two compounds which differed only by one atom of carbon; and in a similar manner the atomic refractions of the remaining elements were determined.

With the aid of these constants it was now possible to calculate *a priori* the molecular refraction of many organic compounds from the elements composing them, and Landolt showed that the calculated molecular refractions agreed very well with those determined by experiment.

§ 8. Gladstone, in the course of his researches, was able to confirm Landolt's results in many cases. But he also found a considerable number of substances in which the observed molecular refraction was completely at variance with that obtained by adding the atomic refractions together. The exceptions were so numerous, that they really seemed to overthrow the whole law of summation.

## IV.

§ 9. Shortly before 1880, when I was studying the literature of chemical optics, a brief note published by Gladstone in the *Journal of the Chemical Society* for May 1870, excited my attention and curiosity. The author there discusses the exceptions to Landolt's rule of summation. He shows firstly that in all such cases the molecular refraction is never found to be too small, but always too great. Then he shows that whole classes of compounds behave in this abnormal fashion.

§ 10. All optically abnormal compounds proved to be rich in carbon. Gladstone, therefore, examined the effect which a gradual increase of carbon in the composition of a body exerted on its refractivity. He found that there actually was an increase in the excess of the experimental as compared with the calculated molecular refraction, but the increase was not regular enough to explain the anomalies.

The saturated hydrocarbons, or *paraffins*, of the general composition  $C_nH_{2n+2}$ , showed *normal* molecular refraction.

Also the *olefines*, containing two atoms less of hydrogen, were found normal by Gladstone.

On the other hand, the hydrocarbons containing six atoms less of hydrogen, viz., the *terpenes*, gave molecular refractions about 3 units larger than would correspond to their composition.

With the aromatic hydrocarbons, such as benzene, toluene, etc., containing eight atoms less of hydrogen, this abnormal excess amounted to 6 units :—

Paraffins	. . . .	$(C_nH_{2n+2})$	Normal
Olefines	. . . .	" $-H_2$	"
Terpenes	. . . .	" $-H_6$	" +3
Benzene and Derivatives	. . . .	" $-H_8$	" +6

With still further decrease in the quantity of hydrogen contained (i.e. with further increase of carbon), there resulted greater and greater refractive increments.

The last member of the series, however—pure carbon without any hydrogen, represented by the diamond—proved to be perfectly normal in its optical properties.

## V.

§ 11. François Arago, when sketching in his celebrated "Éloges" the life and work of Thomas Young, relates that the latter was led to his fundamental discovery of the interference of light by nothing more extraordinary than soap-bubbles. In this connexion Arago remarks that it is one of the most precious gifts to be able to wonder at the right time.

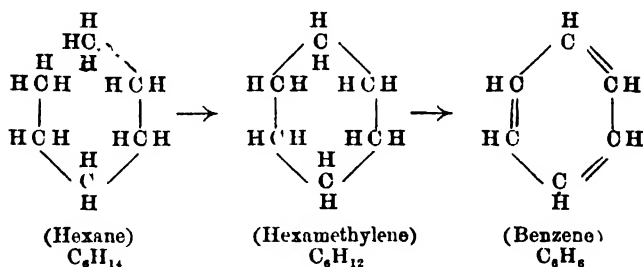
Gladstone's observations just mentioned had been known almost

ten years without anybody's surprise being excited. When his short note came into my hands, I was fortunate enough to begin wondering at the right time.

It seemed to me really extraordinarily remarkable that all optically abnormal substances, without exception, gave a too *high* molecular refraction. It was no less astonishing to me that the saturated hydrocarbons were optically normal, but became more and more abnormal at successive withdrawals of hydrogen—while pure carbon, uncombined with hydrogen, is again completely normal.

But I was most particularly struck by the quantitative amount of the abnormality in the case of benzene compounds, especially their refractive increment of *six* units. The number 6 fascinated me. I could not help thinking that therein lay the key to the mystery, and I lost no time in making use of it.

§ 12. According to Kekulé's ingenious hypothesis we can imagine benzene,  $C_6H_6$ , to have arisen from the saturated hydrocarbon hexane,  $C_6H_{14}$ , by successive removal of hydrogen.



Thus altogether four pairs of hydrogen atoms have been removed. The elimination of the first pair was made the occasion to form another *simple* carbon bond, like those already present in hexane, and with it the ring was closed. The splitting-off of the other three pairs of hydrogen atoms, on the other hand, resulted in the formation of three *double* bonds of carbon atoms—a kind of bond which does not occur in the optically normal hexane.

Now Gladstone had found that benzene exhibits a refractive increment of 6 units. Reading this I was struck in a moment by the thought: might not this abnormal refractive increment of benzene be due to its double carbon bonds, which are absent in the optically normal hexane?

And if this were so, I went on to reason, since *three* double bonds in benzene correspond to a refractive increment of 6 units, therefore *one* double bond must entail the increment of 2.

These ideas received no support whatever from the then known facts. For Gladstone had stated expressly that the olefines, i.e. open-chain hydrocarbons, containing *one* double carbon bond, were optically *normal*.

However, I did not allow myself to be discouraged ; and, behold ! my expectations were confirmed by the very first experiment. The olefine examined not only proved to be optically abnormal, but gave the predicted refractive increment of 2 units, corresponding to the presence of *one* double carbon bond.

Gladstone, therefore, as I had supposed, was mistaken in this case. Further experiments proved that not one of the olefines was optically normal. Without exception they gave the refractive increment of 2 units, one-third of that of benzene.

I next proceeded to examine the diolefines—substances which contain *two* double carbon bonds. Here also, in conformity with expectation, a constant refractive increment was found, double as large as that of the olefines and two-thirds of that of benzene :—

Paraffins . . . .	( $C_nH_{2n+2}$ )	Normal	
Olefines . . . .	" - $H_2$	"	+ 2
Diolefines . . . .	" - $H_4$	"	+ 4
Benzene compounds . .	" - $H_8$	"	+ 6

The dimensions of our subject this evening prevent the detailed demonstration of these important facts by experiment. I will only show you that the spectrum of a saturated hydrocarbon (a paraffin) is distinguishable at a glance from that of a substance containing double bonds.

On this screen we project the electric spectrum of metallic calcium. First we cause the rays of light to pass through a prism filled with paraffin-oil. Then we exchange this prism for another, filled with a substance containing atoms linked by double bonds. (Experiment.)

In the second case you observe, firstly, a much greater deviation of the whole spectrum, i.e. greater *refraction*, and secondly, far wider intervals between the coloured lines of the spectrum, i.e. greater *dispersion*, which is usually correlative to the refraction.

§ 13. Thus quantitative experimental confirmation was obtained for the view that abnormal refractive increments which increase with the diminution of hydrogen contained in the substances, are caused by the presence of double carbon bonds.

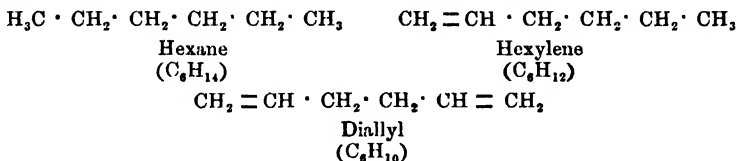
At the same time, however, the experiments yielded a second result of fundamental importance. The olefines contain 2, and the diolefines 4 atoms of hydrogen less than the paraffins. Similarly the refractive increment of the olefines is 2, and of the diolefines 4.

Benzene,  $C_6H_6$ , contains 8 atoms of hydrogen less than the corresponding paraffin, hexane,  $C_6H_{14}$ . The increment of benzene, however, amounts not to 8, but to 6 ! Thus in the formation of benzene from hexane, 2 atoms of hydrogen have been eliminated without influence on the refractive increment of the product.

But in the formation of benzene from hexane, 2 atoms of hydrogen have been employed to close the ring (see diagram on p. 126).

The withdrawal of these two atoms and the closing of the ring have therefore taken place without causing any optical anomaly.

In the formation of the olefines and diolefines from the paraffins, however, there is no closing of the ring. These substances are of open-chain structure, and *every* removal of 2 hydrogen atoms corresponds here to the creation of a double carbon bond :—



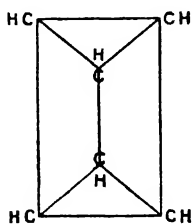
Hence, also, the refractive increment of the olefines and diolefines is directly proportional to the number of hydrogen atoms removed from the paraffin.

From all this it follows that the removal of hydrogen atoms causes optical anomalies only where double carbon bonds are created by the process. *The splitting-off of hydrogen which results in a closing of the ring is, on the other hand, without abnormal optical influence, and produces no refractive increment.*

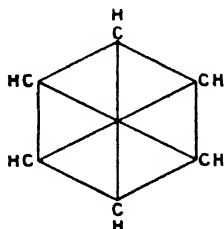
This latter principle, which has since been confirmed many times by experiment, has proved of the same importance as the first in the investigation of the chemical structure of bodies.

§ 14. A few examples will show how these two principles can be utilised for the discovery of chemical structure.

Besides the formula already mentioned for benzene—that suggested by Kekulé—several others have been proposed, e.g. those by Ladenburg and Claus :—



(Ladenburg)



(Claus)

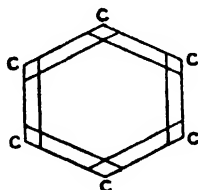
Neither of these graphic formulæ is reconcilable with the results of spectro-chemical investigation, because the neighbouring carbon atoms contained in them are associated only by single cycloid or ring-closing affinities, and not by any so-called double bonds. Substances of this kind should be optically normal, while benzene and its derivatives are as a matter of fact abnormal. Kekulé's formula

for benzene is really the only graphic representation of its structure in a single plane which is confirmed by chemical optics.

Thus it can be at once determined by optical methods whether a given body belongs to the paraffinoid, olefinoid, or cycloid products ; whether these products contain double bonds or not ; and if so, how many.

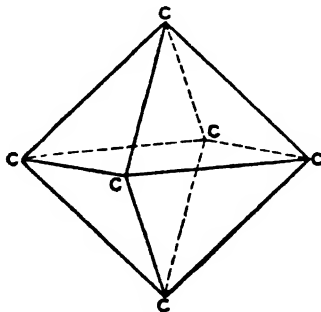
Now, too, we can imagine why the diamond, i.e. pure crystallised carbon, is, as already mentioned, optically normal. We obtain an idea of the mineral's chemical constitution, and of the way in which the atoms of carbon are perhaps combined in the sparkling gem.

For the reasons already stated, the diamond cannot possibly contain any double bonds ; a combination, say, in the form



with one atom of carbon at each of the six corners, and with each atom connected with its neighbour by a double bond, is altogether impossible.

Imagine, however, at each of the six corners of a regular octahedron, a single molecule of marsh-gas,  $\text{CH}_4$ , i.e. altogether  $\text{C}_6\text{H}_{24}$ , and then imagine all the 24 hydrogen atoms successively removed, so that each carbon atom is connected with each of its neighbours only by a single bond, and thus all six atoms of carbon are united together in a single whole. Then you obtain, as the most simple representation of the molecule of the diamond, a regular octahedron, with one atom of carbon at each of its six corners, while the edges represent the mutual bonds :—



Several simple molecules of this kind may be combined into one crystallised particle of the spectrochemically normal diamond.

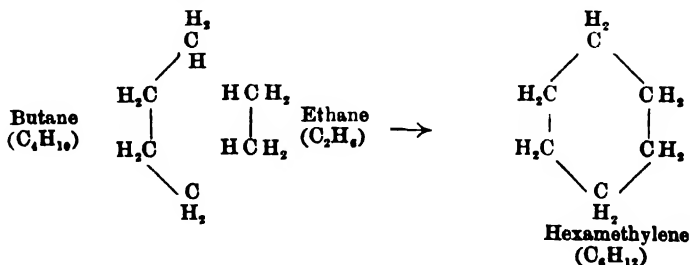
§ 15. Thanks to the explanation of the optical behaviour of benzene, with the resultant discoveries, it all at once became possible to understand the causes of the spectro-chemical abnormality of whole classes of bodies, such as the olefines, diolefines, terpenes, aromatic compounds, etc., and light was cast on the chemical constitution of whole classes of bodies.

At the same time, however, it at once became apparent why both Landolt and Gladstone had succeeded in observing complete optical normality in very numerous substances of the most various types—alcohols, acids, ethers, hydrocarbons, etc. And now it was understood why in such bodies the molecular refraction is determined solely by the component elements, while the different grouping of the atoms, i.e. the isomerism, remains without any appreciable optical influence.

All the bodies of this kind proved to be either paraffins, i.e. saturated hydrocarbons, or simple derivatives of the same. But the paraffins, as we now know, are always optically normal, because they contain no double carbon bonds. For this reason all such simple derivatives of the paraffins must also be normal. Their molecular refraction will thus always correspond to the elements of which they are composed, however the atoms may be grouped, i.e. chemical isomerism is here also without influence.

§ 16. For the same reason, however, all cycloid (ring-shaped) closed formations, if they contain no double carbon bonds, must be optically normal, for those bodies also may be conceived as originating in the simple replacement of hydrogen by paraffin fragments, and may therefore be regarded as combined paraffins.

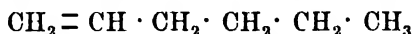
Thus we can imagine the hexamethylene already mentioned not only as formed from hexane by removal of *two* hydrogen atoms from the ends, but also as arising from ethane and butane, i.e. from two paraffins, by the removal of *four* hydrogen atoms and welding together of the remains :—



As a combined paraffin, hexamethylene must be normal, as is also confirmed by experiment, and here we see again, as in the case of the

diamond, that a progressive removal of hydrogen and increase of carbon need not lead to the slightest optical anomaly.

At the same time there arises here a case of the optical influence of isomerism, for hexylene, which has already been mentioned, with the same formula ( $C_6H_{12}$ ) as hexamethylene, but in structure an olefine :—



possesses the familiar refractive increment of 2 units. This example again shows how the spectro-chemical behaviour of a body discloses its chemical structure by enabling us to distinguish with certainty between an optically normal cycloid (or ring-substance), and an isomeric open-chain olefinoid formation, which is optically abnormal.

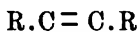
## VI.

§ 17. Carbon can thus act variously upon light according to the manner in which its atoms are combined. We can therefore transfer the refractive increment of the double bond to the atom itself.

In the diamond, and in all paraffinoid carbon compounds, the atomic refraction of carbon equals 5 ; it is therefore equal to 10 for two carbon atoms. The double bond increases the refraction by 2, so that for two carbon atoms with a double bond the refraction amounts to 12. The atomic refraction of *one* carbon atom with a double bond is therefore equal to 6, i.e. 20 per cent. greater than that of the atom with the single bond :—

	Atomic Refraction
1 Carbon atom C (diamond and paraffins) . . . . .	5
2 Carbon atoms 2C (diamond and paraffins) . . . . .	10
Double bond . . . . .	2
2 Carbon atoms with a double bond $C \equiv C$ . . . . .	12
1 Carbon atom with a double bond $C =$ . . . . .	6

§ 18. Carbon, being a quadrivalent element, can also appear with *triple* bonds :—



Experiment has shown that carbon with a triple bond also acquires a special atomic refraction.

Thus it becomes possible to establish the presence of this kind of bond in substances, and to distinguish it from the double and simple bonds—a further criterion of structure.

§ 19. In consequence of these discoveries it became highly probable that all multivalent elements, such as carbon, possessed an atomic refraction varying with the kind of bond, while the univalent elements, such as hydrogen, display constant optic values because atoms such as theirs can only be linked with a simple bond.



Later researches have confirmed this. The univalent halogens give, like hydrogen, constant atomic refractions, both in the elementary state and in their compounds. The multivalent elements, on the other hand, such as oxygen and nitrogen, display different optical values, according to the kind of bond.

In the course of such researches the behaviour of oxygen as a quadrivalent element, which had been previously conjectured, was established with certainty, and afterwards confirmed synthetically by Collie, Tickle, and others.

§ 20. The theory which accounted for the optical abnormalities of certain classes of bodies, making them in fact abnormalities no longer, has proved extraordinarily fruitful. It formed the starting-point of all subsequent discoveries in the subject, and indeed we may describe the progress of this branch of science during the last 25 years as based essentially on this conception.

For not until we had fathomed the mystery of the benzene refractive increment  $\delta$ , was it possible to know for certain that the variable valency of the multivalent elements is always of determining influence on the optical behaviour of bodies. Thus for the first time a spectrochemical method was called into being for the study of chemical structure, and the foundations were laid of what we now call "Spectro-chemistry."

## VII.

§ 21. We must now return once more to the formula for refractivity. Newton's expression  $\left(\frac{n^2-1}{d}\right) P$  had proved not constant for the temperature in the case of fluid bodies, and was, therefore, replaced by Gladstone and Dale's more satisfactory ratio  $\left(\frac{n-1}{d}\right) P$ .

For 20 years and more this did admirable service. As, however, the number of observations kept on increasing, even this formula betrayed imperfections which finally led to its abandonment. It is impossible here to follow the argument in detail, and we must be content with the remark that comparisons of bodies in different states of aggregation failed to yield satisfactory constants. The values of  $\left(\frac{n-1}{d}\right) P$  for a fluid or solid substance always came out considerably greater than for the same substance in the state of gas or vapour.

§ 22. Then by a happy chance two physicists, L. Lorenz, of Copenhagen, and H. A. Lorentz, of Leyden, came forward simultaneously in 1880 with a new expression for refraction. One of them started from the ordinary theory of light, the other from Maxwell's electromagnetic theory of light based on Faraday's views, and they

both reached the same result, viz., that the true measure of refractivity is furnished by the expression

$$\frac{(n^2 - 1)}{(n^2 + 2)} \frac{P}{d}.$$

Experimental tests showed that this theoretical expression was in fact, for all bodies, practically unaffected not only by temperature and pressure, but also by the state of aggregation.

Chemical tests confirmed the utility of the new optical standard, since the operation of all the laws before mentioned was observed to be even more exact when the new constant was applied.

§ 23. Moreover, the expression for refraction proved valuable in another respect. It was found to be very suitable for measuring the *dispersive* power of bodies.

If  $n_v$  and  $n_r$  denote the refractive indices for the limits of the visible spectrum, i.e. for violet and for red light, the difference of the refractivities for these end-rays of the spectrum :

$$\left( \frac{n_v^2 - 1}{n_v^2 + 2} - \frac{n_r^2 - 1}{n_r^2 + 2} \right) \frac{P}{d}$$

is the measure of the power of different bodies to *disperse* light—to broaden out the spectrum. This ratio proved to be constant as regards temperature, pressure, and state of aggregation.

Gladstone had already observed that dispersion, like refraction, was connected with the chemical nature of bodies. Quantitative relations were, however, only obtained when a constant for refractivity had been found. And then from the molecular dispersions of compounds the atomic dispersions of their elements were deduced.

We cannot enter here into the relations which were thus shown to exist between the chemical composition of substances and their power to disperse light. We need only remark that the case as a whole is analogous to that of refraction. Dispersion is, however, a still more sensitive and more constitutional property, and therefore in many cases it is specially adapted as an aid to research on chemical structure.

### VIII.

§ 24. It only remains to add a few remarks on the applications of spectro-chemistry in science and in practical life.

I have already shown the principles on which spectro-chemical methods of examination in general can be applied to the solution of scientific problems, to the discovery of the chemical structure of single substances or whole classes of bodies.

Now there are a large number of substances, some of them artificially built up by synthesis out of their elements, some of them occurring in the vegetable and animal kingdoms, or even in inorganic nature, the structure of which is of remarkable delicacy and insta-

bility. Among them are, for instance, the so-called "tautomeric" compounds, hydrogen peroxide, and many other unstable compounds. Substances of this kind are of a very special interest, for in consequence of their tendency to change, they are the principal cause of metamorphoses, the unceasing circulation of matter, the eternal birth and decay that goes on in nature.

Research into the atomic structure of such bodies by purely chemical methods is often very difficult, and not seldom impossible, because, owing to their sensitive organisation, chemical interference leads either to changes in the grouping of the atoms, which cannot always be controlled, or even to total decomposition.

In such cases it is of course of the greatest value to be able to examine the constitution of the bodies without affecting them chemically; and spectrochemistry, as we have seen, gives us the means of doing so. By observing the behaviour of light on its passage through the various substances, we gain an insight into their structure without in any way disturbing it.

§ 25. In the last ten years the spectro-chemistry of the nitrogen compounds has also made remarkable progress. Nitrogen is of the greatest importance as an essential constituent of the proteids, the alkaloids, and many other animal and vegetable products. But its high valency and the extraordinary variety of combinations into which it can enter with other elements, surround it with special complications. Regardless of these, however, the spectro-chemical examination of nitrogen compounds has already yielded useful results, especially in the study of the alkaloids. It is to be expected that this optical method will also be of use in the chemistry of the albuminoids, the study of which is now being prosecuted with so much vigour.

§ 26. One class of substances of increasing importance both to science and to chemical industry is that constituted by the natural and artificial perfumes. An overwhelming majority of them consists of derivatives of the terpenes. We have already mentioned that Gladstone, in this subject also a pioneer, was the first to study the optical behaviour of the terpenes. Since then the explanation of the structure of these bodies and of a large number of rich natural perfumes derivable therefrom has been rendered easier by the use of spectro-chemical methods. Similar assistance has been rendered to the synthetic preparation of valuable scents, such as ionone, the artificial scent of violets. In every scientific laboratory and in every rationally conducted chemical factory where work is being done on perfumes, the spectrometer is now an indispensable testing instrument, and hence also an implement in industrial production.

## IX.

§ 27. When scientific research opens up new methods of observing nature, it is generally not long before a use is found for these methods

in practical life. The need is soon felt of perfecting, and at the same time simplifying, the scientific apparatus. Efforts in this direction have not been wanting in the case of the spectrometer, and they have been crowned with the most brilliant success.

Professor Abbe, the distinguished physicist who died not long ago, and after him Dr. Pulfrich, constructed spectrometers on the principle of total reflection. These instruments are distinguished from those formerly in use by their extraordinary simplicity and convenience, and they allow also of much more rapid work.

Such instruments, known as total-reflectometers, have been made for the most exact scientific measurements, and also for medical and technical purposes. Special forms are in use for the examination of fats and oils, milk and butter; to determine the amount of salt contained in salt solutions; the amount of alcohol and extractive matter in beer; for the examination of blood and albuminoids in pathological fluids, etc. Several of these ingeniously contrived instruments give not only the refractive index and the dispersion of a substance immediately, without any calculation, but also directly the percentage of dissolved matter, e.g. of alcohol and extractives in beer.

A number of such instruments from the celebrated factory of Carl Zeiss, of Jena, are here exhibited at my request.

I have now reached the end of my remarks. I have reviewed the development of spectro-chemical research since Newton's time, and we have seen that, although different nations have taken part in the work, a specially large share has fallen to British investigators. For this reason, as I said at the beginning of my discourse, it has been a special pleasure to me to be able to treat of such a subject before the Royal Institution.

There is a saying of Montesquieu's which I venture to hope has its application to this evening: "*Quand vous traitez un sujet, il n'est pas nécessaire de l'épuiser, il suffit de faire penser.*"

From Newton to our own day—a length of time which our planet takes to complete 250 revolutions round the sun—that is the period through which we have sped in 60 minutes. It will be readily understood that on such a rapid trip we have only been able to stop at one or two view-points, and have been obliged to content ourselves with a hasty survey. I thank you all for having ventured yourselves with me on such a hurried excursion, and I shall be happy if it has been conducted without mishap.

[J. W. B.]

Friday, January 19, 1906.

The Right Hon. THE EARL OF ROSSE, K.P. B.A. D.C.L. LL.D.  
D.Sc. F.R.S., Vice-President, in the Chair.

PROFESSOR JOSEPH JOHN THOMSON, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,  
Professor of Natural Philosophy, R.I.

*Some Applications of the Theory of Electric Discharge to Spectroscopy.*

THE luminosity produced by an electric current passing through a gas at low pressure varies greatly in character, not only when we alter the nature of the discharge—as, for example, when we pass from the arc to the spark—but also in many cases at different points of the same discharge. The luminosity may be of one colour at one place and of a very different one at another; a spectroscopic examination shows the spectrum of the same gas often varies considerably as we proceed along the line of discharge. As recent experiments have thrown a considerable amount of light on the processes going on in the different kinds of electrical discharge and at different parts of the same discharge, the study of the connection between the changes in the electrical effects and the changes in the spectra might be expected to throw some light on the very interesting question of the genesis of spectra. Many important points can very conveniently be studied by the aid of Wehnelt's method of producing the current. In this method the cathode is a strip of platinum or a piece of platinum wire on which either a little lime or barium oxide has been deposited. This when heated to redness emits large supplies of corpuscles, and by altering the temperature of the platinum very large variations in the current passing through the tube and the potential difference between the electrodes can be obtained. In our experiments the current has varied from a small fraction of a milliampere to several amperes, and the potential difference from a few volts to several hundred.

The apparatus used is shown in Fig 1. A B is the platinum strip with the line on it; a thermo-couple, a platinum and platinum-rhodium junction, was fused to this strip and served to determine its temperature; the strip was connected with the earth and was heated by a current passing through the leads L, M; a rheostat was placed in series with the heating current and by means of this the temperature could be altered gradually. The anode was a platinum disc; this was connected with the positive pole of a battery of storage cells, the negative pole of which was earthed; to allow of gradual variations in the potential

difference between the electrodes a potential divider of 100 resistances of 10 ohms each was used. The current through the tube was measured by a D'Arsonval galvanometer, and the potential difference between the terminals by a Weston's volt-meter.

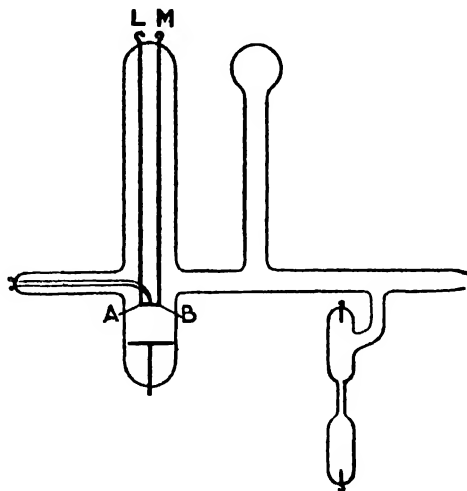


FIG. 1

Some of the most interesting features of the discharge are very prominent when the temperature of the platinum is high, say  $1400^{\circ}\text{C.}$ , and the pressure of the gas low, less than  $\cdot 01$  mm. of mercury. The discharge is light blue, and its spectrum shows the mercury lines and the band spectrum of nitrogen. In this case the relation between the current and the potential difference is represented by a curve like Fig. 2, the ordinates representing the current and the abscissæ the potential difference.  $G$  is the point at which the luminosity begins. In the case we are considering, when the wire is very hot and the pressure low, the change from the dark to the luminous discharge takes place very abruptly, an increase of the potential difference by  $\frac{1}{100}$ th of a volt being often sufficient to convert a discharge, where no light could be detected, even in a darkened room, to one where the light was quite bright. When luminosity appears, there is a very rapid increase in the current; in some of the experiments an increase in the potential difference of  $\frac{1}{100}$ th of a volt increased the current forty-fold. At this stage the thermopile showed that there was no increase in the temperature of the platinum when the luminosity appeared. We shall see later on that it is possible by using large potential differences to get such large currents through the tube that the platinum becomes appreciably warmer by the passage of the current.

One point which I think very suggestive is the abruptness with

which the luminosity round the cathode appears. We see that by a very small increase in the potential difference the discharge passes from a state in which no luminosity can be detected, even in a dark room, to one where the luminosity can plainly be seen in a bright light; thus the molecules of the gas in the tube just when the luminous discharge is on the point of appearing, are in a state in which a very small change in the electrical conditions of the tube make the molecules pass from a state in which they are not giving out an appreciable amount of light to one where they are brightly luminous; and, as the great increase of the current when the luminosity appears shows, this change in state is accompanied by an emission of corpuscles. From this and other considerations, I have come to the conclusion that what takes place when the gas becomes luminous is that the internal energy in the atom in consequence of its bombardment by the corpuscles increases, and when it gets up to a certain critical value the equilibrium of the atom becomes unstable: an explosion occurs, resulting in an expulsion of corpuscles and such a shaking up of those left in the atom that these vibrate so vigorously that the energy radiated is sufficient to produce luminosity. Thus, I regard the ionization of

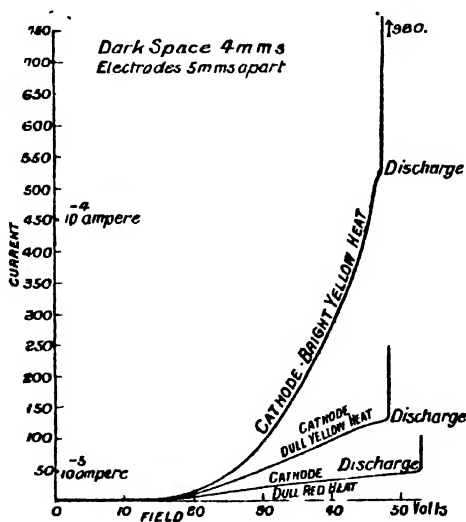


FIG. 2.

the gas as being due, not to the corpuscles in the atom being dragged out by the direct action of the electric forces in the field, or as being knocked out by a rapidly moving corpuscle striking against them, but to an explosion due to the atom having absorbed so much internal

energy that its equilibrium becomes unstable. Other phenomena point to this as the method by which ionization is effected. If the corpuscles are dragged out of the atoms by the electric field, the velocity with which they are projected should depend upon the strength of the field; while, if they are projected by an explosion, their velocity would depend upon the nature of the atom and not upon the strength of the field. Now when Röntgen rays fall upon a substance, the atoms of the substance are ionized, and corpuscles, forming a stream of cathodic rays, are emitted. Barkla has lately shown, however, that the penetrating power of the cathodic rays produced in this way is independent of the intensity of the Röntgen rays. Now the electric force in the Röntgen rays depends upon their intensity, and the penetrating power of the cathodic rays depends upon their velocity; so that this result shows that the velocity of the corpuscles does not depend upon the intensity of the force acting upon them. Again, Lenard has shown that the velocity of the corpuscles ejected when ultra-violet light falls upon a metal is independent of the intensity of the light. Lenard also investigated the secondary cathode rays produced when cathode rays fall upon matter, and found that, in addition to rays, whose velocity was of the same order as that of the primary rays, and which may be regarded as deflected primary rays, there were other very slow rays; and the measurements he gives indicate that the velocity of these varies but little with that of the primary rays.

A point of great importance, which can easily be shown by this apparatus, is that the stage at which luminosity sets in depends upon the current density through the tube, and not merely upon the potential difference. One way of showing this is to lower the temperature of the platinum, keeping all the other conditions the same, and again determine the relation between the current and the potential difference. The effect of lowering the temperature is to reduce the number of corpuscles starting from the cathode, so that with the same potential difference the current density is smaller. If the relation between the current and potential difference are represented by curves, such as those in Fig. 3, it will be seen at once that the curve for the cooler electrode cannot be deduced from that for the hotter by reducing all the ordinates in the same proportion. The critical points on the curves, i.e. the place where ionization by collision begins and where the luminous discharge appears, are at very different potentials: the greater the current density the smaller the potential difference corresponding to these critical points. Thus, to take a case actually observed, when the wire was very hot the discharge was brightly luminous with a potential of 24 volts, but on lowering the temperature no luminosity could be detected with a potential difference of 110 volts.

We can also show the effect of current density without altering the temperature of the cathode, by placing near the tube an electro-



magnet, so arranged that its lines of magnetic force in the discharge tube are along the line joining the cathode and the anode. The effect of the magnetic field is to make the corpuscles move along the lines of force, and thus, without altering the number of corpuscles emitted by the cathode, it concentrates their paths, and so increases the maximum current density in the tube. When the magnet is on, ionization by collision and luminosity both occur at a much lower potential difference than when it is off, and it is easy to arrange matters so that keeping the potential difference constant, the discharge is luminous when the magnet is on and dark when it is off. When the potential difference is too small to produce a bright discharge even when the

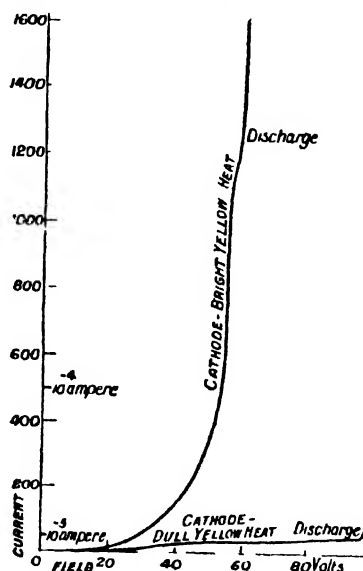


FIG. 3.

magnet is on, the current through the tube is often greater when the magnet is on than when it is off. By placing the magnet so that the lines of magnetic force are across the line joining the cathode to the anode, we can render the paths of the corpuscles more diffuse than they would be without the field, so that the maximum current density is less when the magnet is on than when it is off. In this case it requires a larger potential difference to produce a luminous discharge with the magnet on than with it off. Similar effects produced by a magnet on another kind of discharge are described in my "Recent Researches," page 105.

The potential difference  $P$ , just when the glow commences, when

the pressure is low, sometimes varies so rapidly with the current  $i$  as to be roughly inversely proportional to it. The following are some values of  $i$  and  $P$  for a gas at a constant low pressure as the temperature of the platinum strip was increased. The numbers are in the order of increasing temperature :—

$i$ (in scale divisions)	$P$ (volts)	$Pi$
6 . . . . .	30 . . . . .	360
8.7 . . . . .	40 . . . . .	346
11.2 . . . . .	30 . . . . .	336
14 . . . . .	25 . . . . .	350

Such a simple relation between  $P$  and  $i$  is, however, exceptional.

The fact that the potential differences at which ionization by collision, or luminosity begin depend upon the current density, shows that the ionization or luminosity of an atom need not, and indeed cannot entirely, be the result of a *single* collision between a corpuscle and the atom. For if that were the case, then, since the energy of the corpuscle depends only upon the electric field and not upon the current density, the effect of increasing the current density would merely be to increase in the same proportion the number of luminous atoms, while as a matter of fact if the potential difference is kept constant and the current increased by raising the temperature of the platinum strip, the increase in the luminosity is greater out of all proportion than the increase in the strength of the current.

The result however, is easily explained if we look at the question from the following point of view. Suppose that for ionization or luminosity to take place the internal energy of the atom must increase by certain amounts, say  $E_1$ ,  $E_2$  respectively. Then, if the energy possessed by the corpuscle were very great, the result, of one collision with an atom might be to give to the atom enough energy to ionise it or make it luminous, or both. But even if the corpuscle were less energetic, and did not in one collision give enough internal energy to the atom to ionise it, it would communicate some energy to it; and if the atom had any power of storing up energy, this would form a contribution towards the critical amount of energy required by the atom before it is ionised. The atom, after having had this energy communicated to it, would not, as long as it retained any of it, require so much energy to ionise it as before. The atom, too, might acquire energy, not merely by corpuscles striking against itself, but also by the collision of corpuscles with neighbouring atoms. Such collisions generate soft Röntgen rays, the energy of which might be absorbed by the atom under consideration, and help to raise its energy to the critical point. The energy in the Röntgen rays might by itself raise the internal energy of the atom to this value, or else raise it so nearly to this value that the collision with a corpuscle would give it enough energy to carry it past the critical stage. The rate at which the energy, due to collisions of corpuscles with itself or with

neighbouring atoms, comes to an atom will be proportional to the rate at which energy is being communicated to the gas, i.e. to  $F \times i$ , where  $F$  is the electric force and  $i$  the current density; and thus for a constant electric force would be proportional to the current density. The atom will radiate away some of its internal energy; if the rate of this radiation is proportional to the amount of energy  $E$  possessed by the atom, say equal to  $\beta E$ , then if  $q$  is the rate at which energy is being communicated to the atom, we have

$$\frac{dE}{dt} = q - \beta E$$

so, if  $E$  vanishes with  $t$ ,

$$E = \frac{q}{\beta} (1 - e^{-\beta t})$$

Thus  $q/\beta$  is the limit to the energy acquired by the atom, and this is proportional to  $q$ , while  $q$  is proportional to  $F i$ ; so that the atom will acquire the critical amount of energy, or not, according as  $F i$  is greater or less than a certain value.

*Application of these Results to Spectroscopy.*—We have seen that the passage from the dark to the luminous discharge occurs with great abruptness, an increase of the potential difference by  $\frac{1}{100}$ th of a volt being sufficient under certain circumstances to convert a discharge in which no luminosity at all could be detected to one where it was quite bright. This suggests that the luminosity sets in when the internal energy of the atom -- or rather of that part of it which gives rise to the particular kind of light present in the luminous discharge -- attains a perfectly definite value. This way of regarding the origin of the luminosity affords a very simple explanation of the variation of the spectrum with the kind of discharge, and of the effect of introducing capacity or self-induction into the circuit containing the discharge tube. Let us consider the rise in energy of a vibrating system inside the atom. Let  $E$  be the energy at the time  $t$ ;  $\alpha$  the rate at which it is absorbing the work done in the discharge tube. The energy may be supplied to it from the Röntgen radiation in the tube, or from the corpuscles which come into collision with the atom:  $\alpha$  will be proportional to the rate at which the electric field producing the discharge is doing work in the neighbourhood of the atom we are considering. It will thus be proportional to the product of the electric force and the flux of corpuscles in this neighbourhood. Let us suppose that the system radiates energy at a rate proportional to  $E$ , say equal to  $\beta E$ ; then we have

$$\frac{dE}{dt} = \alpha - \beta E$$

$$\text{or } E = \frac{\alpha}{\beta} (1 - e^{-\beta t})$$

if  $E = 0$  when  $t = 0$ ,

Consider two different systems A and B in the same atom. Let  $E_1, \alpha_1, \beta_1$ ;  $E_2, \alpha_2, \beta_2$  be the values of  $E, \alpha, \beta$  for the systems A and B respectively:—

$$E_1 = \frac{\alpha_1}{\beta_1} (1 - e^{-\beta_1 t})$$

$$E_2 = \frac{\alpha_2}{\beta_2} (1 - e^{-\beta_2 t})$$

Now suppose that the system A is one that does not absorb much, but also does not radiate much, while B absorbs a great deal more than A, but radiates still more in proportion, so that  $\alpha_2 > \alpha_1$ , but  $\alpha_1/\beta_1 > \alpha_2/\beta_2$ , so that ultimately  $E_1$  is greater than  $E_2$ , but at first  $E_2$  is greater than  $E_1$ . The curves (1) and (2), Fig. 4, represent the variations of  $E_1$  and  $E_2$  with the time.

Suppose now that systems A and B become luminous when the internal energy is equal to  $W$ . It is not necessary to assume that the critical amount of energy is the same for the two systems, the assumption is only made to simplify the diagram, the reader will see that the argument would apply if the critical amounts of energy were different in the two cases.

Now consider first the case when the rate at which work is being done in the tube is so small that though  $\alpha_1/\beta_1$  is greater than  $W$ ,  $\alpha_2/\beta_2$  is less than  $W$ , the case represented in Fig. 4; here system A acquires the amount of energy necessary to make it luminous, while system B does not; thus in this case the spectrum of the gas would show the lines corresponding to A but not those of B. Suppose now

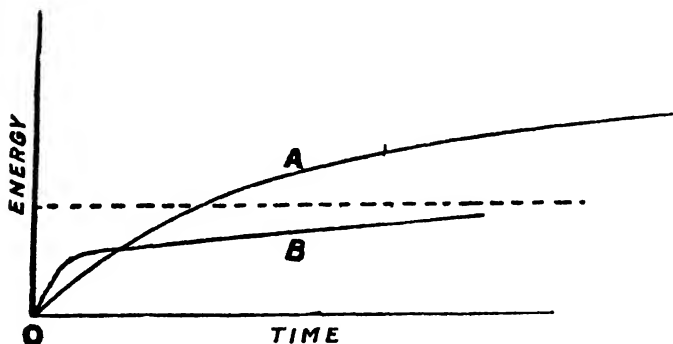


FIG. 4.

we increase the rate at which work is done in the tube, so that both  $\alpha_2/\beta_2$  and  $\alpha_1/\beta_1$  are greater than  $W$ , the case represented in Fig. 5.

Here the system B attains the critical amount of energy, and it reaches this value before A does, so that in this case the lines of B

will be visible. Let us now consider the lines in the spectrum corresponding to the system A; these will be visible if the energy in the system reaches the critical value; the conditions in this case are in some respects more unfavourable for the supply of energy to this

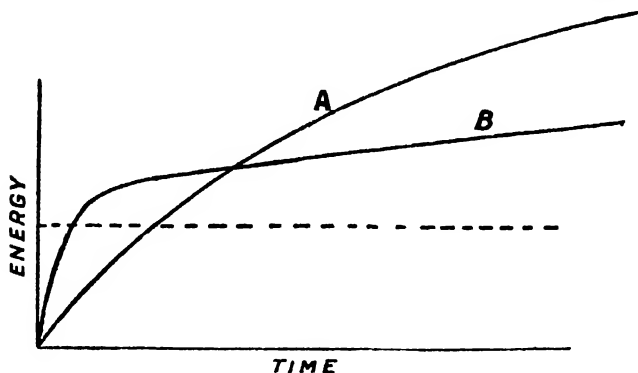


FIG. 5.

system than they were in the previous one. For in the first case the system B got into the condition in which it radiated as much energy as it received, and thus did not absorb any of the energy; in the second case, however, B became luminous before its radiation was equal to the absorption; it is thus taking in more energy than it gives out, and this may result in a diminution in the rate of supply of energy to A; it would do so, for example, to a marked extent if the conditions were such that A received a considerable portion of its supply of energy from B. This diminution in the supply might be great enough to prevent the internal energy in B reaching the critical value. Thus the result of the increase in the rate of supply of the electrical energy might be to weaken or even obliterate the lines of A, and while with the smaller rate we had the lines of A and not those of B, with the larger rate we might have the lines of B and not those of A. Thus an increase in the rate at which the electric field is doing work, such as would be produced by increasing the current through the discharge tube, might result in an entire change of the spectrum. We should expect that it would only be in exceptional cases that the lines of A would be obliterated under the conditions holding in case A, but in all cases the increase in the brilliancy of the lines of B would be large compared with the increase of those in A.

We see from the equations giving  $E_1$  and  $E_2$  that until the supply of energy has lasted for a time comparable with  $1/\beta_2$ ,  $E_2$  is large compared with  $E_1$ ; thus for electrical discharges which last for an exceedingly short time we might easily have the lines of B visible and not those of A.

In a discharge tube conveying an electrical current, the amount of work per unit volume of the gas done by the electrical forces per unit time varies very largely from one point of the tube to another. If the cross section of the discharge is the same at all parts of the tube, so that the current density is uniform, the rate at which the electrical forces do work will be proportional to the electric force. As this is much greater near the cathode than at other parts of the tube, we should expect the lines of systems of the type B to preponderate near the cathode, and to be absent or much feebler in other parts of the tube. If the tube were of the type frequently used for spectroscopic purposes, with a capillary portion in the middle, then, since the current density is much greater in this portion than in any other, the rate of work per unit volume of the gas will be much greater in the capillary portions than in the wide parts of the tube, and we should therefore expect the lines of systems of the type B to be much more prominent in the capillary part than in the wide part.

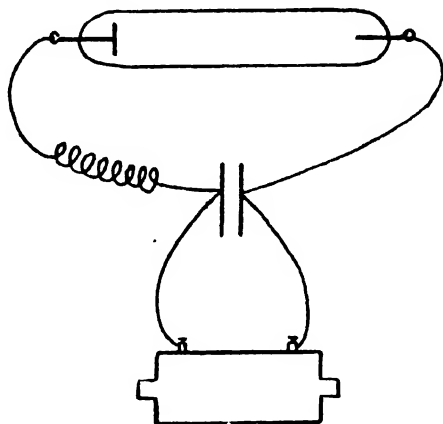


FIG. 6.

*Effect of Self-induction and Capacity.*—Suppose that we have a tube of uniform bore arranged as in Fig. 6, the terminals of the tube being connected with the plates of a condenser of capacity  $C$ , and that there is a coil whose coefficient of self-induction is  $L$ , placed in series with the tube; then if the discharge through the coil begins when the potential difference between the plates of the condenser is  $V_0$ , the potential difference between the plates after a time  $t$  will be

$$V_0 \cos pt$$

and the current through the tube

$$C V_0 p \sin pt$$

where  $p = \frac{1}{\sqrt{LC}}$ .

Thus the maximum value of the product of the current and the potential difference, i.e. rate at which the electric forces are doing work in the tube, is  $C V_0^2 p$ , or  $\sqrt{\frac{C}{L}} V_0^2$ , and is thus proportional to the square root of the capacity and inversely proportional to the square root of the self-induction. Thus, increasing the capacity increases the maximum rate of work and therefore increases the brilliancy of the lines corresponding to systems of the type B relatively to those of type A, while inserting self-induction in the circuit increases the brilliancy of those of type A as compared with those of type B. If we suppose that the "blue" spectrum of argon corresponds to a system of type B, the red to a system of type A, we have an explanation of the changes in the spectrum of this gas, for by inserting capacity in the circuit we can change from the red to the blue spectrum, while having got the blue we can get back to the red by inserting self-induction as well as capacity. I have here a little model which is intended to illustrate the way in which the red and blue spectra of argon originate. It is based on the fact that when we send a current of electricity through a circuit, the current does not rise to its steady value instantaneously, but, starting from zero, increases with the time in exactly the same way as we have supposed the intrinsic energy in the atom, i.e. the way represented by the curve in Fig. 4. The quantity in the electrical case corresponding to the radiation  $\beta$  is the resistance of the circuit divided by the self-induction, while the quantity  $\alpha$  is inversely proportional to the self-induction. Thus, a circuit with large self-induction and small resistance is analogous to the system A, while one with small self-induction and large resistance is analogous to a system of type B. Now my model of the argon atom consists of two circuits, C and D, placed in parallel. C has large self-induction and small resistance, D has little self-induction but large resistance. An electric lamp is placed in each circuit. If I supply energy in one way, i.e. by continuous current to the system, the red lamp in C lights up and the blue lamp in D is dark, while if fed by an alternating current, the blue lamp shines and the red is dark. It would be interesting to see whether, as we gradually diminish the self-induction, we get the whole of the lines in the blue spectrum at once, or whether the lines of this spectrum enter in groups one after the other. I have tried somewhat similar experiments with the hot lime cathode to see in a mixture of gases (mercury vapour and air) which spectrum first appeared as the rate of doing work in the gas was gradually increased. The great difficulty in this determination is that when once the luminosity begins there is such a rapid increase in the ionization that the current through the gas and the rate of doing work increase in an exceedingly short time through a wide range of values, and thus a gradual increase in the rate of work is exceedingly difficult to obtain; on several occasions, however, I was convinced that on gradually increasing the rate of work, the mercury

lines were the first to appear, and were the last to disappear, when the rate of work was reduced from a high value, at which both the nitrogen and mercury spectra were bright down to a point where the discharge ceased to be luminous.

The preceding considerations have also an important application to the difference between the arc and spark spectra. In the continuous arc discharge, although the average rate of work is much higher than in the spark, the maximum rate is very much less; in the spark discharge we have exceedingly intense current density lasting for a very short time, and while the spark is passing we have a very much greater rate of work than in the arc. Hence the state of things in the spark will be analogous to that represented in Fig. 5, and the lines corresponding to systems of the type B will be enhanced relatively to those of type A; we conclude then that the arc lines correspond to systems of the type A, the spark lines to those of type B.

The work done in the discharge tube is probably ultimately converted for the most part into heat, so that the rate at which work is being done at any part of the tube is approximately proportional to the rate at which heat is being produced in the tube. I do not, however, regard temperature, i.e. the energy due to the translation of the atoms as a whole, as having any direct connection with the production of spectra. The work done by the electric field on the corpuscles is, since the corpuscles can easily penetrate the atoms of the gas, first converted into internal atomic energy. This energy may ultimately be for the most part transformed into the energy of translation of the molecules of the gas and so appear as temperature, but it by no means follows that, if we heated the molecules of the gas by non-electrical means to the temperature to which even a few of its molecules are raised by the electric discharge, that we should get a luminous spectrum. The production of the spectrum depends upon the internal energy of the atom. When we use the electric discharge, all the work done by the corpuscles goes at first into the form of internal atomic energy, while if we supplied the same amount of energy to the gas by thermal, as distinguished from electrical means, the energy would go first into increasing the energy of translation of the atoms, and very little of it would ever get inside the atom. It is probable, however, that some of the energy of translation would get converted into internal energy, and that temperature is one way of giving internal energy to the atom and so producing luminosity. From one point of view, however, it is a very extravagant method, as the fraction of the energy spent in heating the gas which goes in producing luminosity is small.

The coefficient of absorption  $\alpha$  of the systems will depend upon the way in which the internal energy is given to the atom, as well as upon the rate at which the electric field is doing work in the neighbourhood of the atom. Thus, for example, if the internal work is given by means of rapidly moving corpuscles, the coefficient of



absorption will depend upon the velocity of the corpuscle, for we can easily show that when a corpuscle passes at a fixed distance from a system of corpuscles having a definite period of vibration, there is one velocity of the corpuscle, depending on this period—fast if the period is short, slow if it is long—for which the energy given by the corpuscle to the system is a maximum. Thus the relation between the amounts of energy absorbed by two systems from the corpuscles depends upon the velocity of the corpuscle. The velocity of the corpuscles in a discharge tube depends upon the pressure of the gas, so that even though the rate at which the electrical forces are doing work may be the same at two different pressures, the relative intensities of the lines of two systems A and B may be different.

Again, we might expect that the coefficient of the rate of absorption of energy would be different according as the energy is given to the atom by means of the large systems which form the positive ions, or by means of small corpuscles; and that the relative brightness of lines might be different in the two cases. In the Canal-Strahlen we have positive ions moving through gas and producing luminosity, and the spectrum of this luminosity possesses interesting peculiarities differentiating it from the spectrum of other parts of the tube. Perhaps the most striking difference, however, is when the positive ions strike against a salt like lithium chloride: they make the red lithium line appear with great brilliancy, while if corpuscles strike against the chloride the red line is not visible. It is remarkable that the spectrum of the metal is produced much more readily by the positive ions when they strike against a salt of the metal than when they strike against the metal itself. This is shown in a striking way, if we take the liquid alloy of sodium and potassium and direct a stream of Canal-Strahlen upon it the clean parts of the alloy appear quite dark, but the specks of oxide scattered over its surface shine with a bright yellow light, giving the sodium spectrum.

When the internal energy of the atom is increased by means of light, as in Professor Wood's beautiful experiments on the fluorescence of sodium vapour, the coefficient of absorption of a system will depend upon the relations between the periods of that system and the period of the light vibrations incident upon them. Thus, as Professor Wood found to be the case, the numerous lines in the spectrum given out by the vapour alter greatly in character and wave-length when the period of the incident light is changed.

The same principles which explain the variation in the intensities of the spectra given out by two different systems in the same atom, can be applied to explain the variations in the intensities of the spectra of two gases A and B when these are mixed together. We know that under some conditions the lines of only one constituent of the mixture appear, while under others we get the lines of both the gases. Let us suppose that the lines of A appear with a lower rate of work of the electric forces than those of B, and that we send a

constant current through the discharge tube. We can calculate what the electric force must be to produce from the molecules of A alone the number of ions required to carry this current; having found the electric force on this supposition, we can, knowing the current, find the rate at which the electric forces would be doing work in the tube. If this rate of work is less than that required to make B luminous, the current will be carried by the ions of A alone, and the spectrum of B will not be developed; if the rate of work on this supposition is greater than that required to make B luminous, the spectrum of B will appear, and it must take a share in carrying the current. Let us suppose that we have so much of A present that the rate of work is not sufficient to develop the spectrum of B, and consider what will happen as the proportion of A is diminished. In order to supply the number of ions required to carry the given current from the smaller number of molecules of A, the electric force, and therefore the rate of work in the tube, must, on the supposition that the current is wholly carried by A, increase, and if we continually diminish the amount of A present, the rate of work will at last reach a value sufficient to make B luminous, with the given current. This stage will give the smallest quantity of A which can, for the given current, wholly swamp the spectrum of B. The rate of work done in the tube will depend on the current going through it, and also on the pressure of the gases, so that both these quantities will influence the proportion of the gas B required to make its spectrum visible.

[J. J. T.]

Friday, February 2, 1906.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR SILVANUS P. THOMPSON, D.Sc. F.R.S. *M.R.I.*, Principal  
and Professor of Physics in the City and Guilds Technical College.

*The Electric Production of Nitrates from the Atmosphere.*

As the demand of the white races for wheat as a food-stuff increases, the acreage devoted to wheat growing increases, but at a less rapid rate; and being limited by climatic conditions will, in a few years, perhaps less than thirty, be entirely taken up. Then, as Sir William Crookes pointed out in his Presidential Address in 1898, there will be a wheat famine, unless the world's yield per acre (at present about 12·7 bushels per acre on the average) can be raised by use of fertilizers. Of such fertilizers the chief is nitrate of soda, exported from the nitre beds in Chili. The demand for this has risen from 1,000,000 tons in 1892 to 1,543,120 tons in 1905; and the supply will at the present rate be exhausted in less than fifty years. Then the only chance of averting starvation lies, as Crookes pointed out, through the laboratory.

In 1781, Cavendish had observed that nitrogen, which exists in illimitable quantities in the air, can be caused to enter into combination with oxygen, and later he showed that nitrous fumes could be produced by passing electric sparks through air. Although this laboratory experiment had undoubtedly pointed the way, though the chemistry of the arc flame had been investigated in 1880 by Dewar, and though Crookes and Lord Rayleigh had both employed electric discharges to cause nitrogen and oxygen to enter into combination, no commercial process had been found practical for the synthesis of nitrates from the air, until recently.

After referring, in passing, to the tentative processes of Bradley and Lovejoy, of Kowalski, of Naville, and to the cyanamide and cyanide processes, attention was directed to the process of Birkeland and Eyde, of Christiania, for the fixation of atmospheric nitrogen, and their synthetic production of nitrates, by use of a special electric furnace. In this furnace an alternating electric arc was produced at between 3000 and 4000 volts, but under special conditions which resulted from the researches of Professor Birkeland; the arc being formed between the poles of a large electro-magnet, which forced it to take the form of a roaring disc of flame. Such a disc of flame was shown in the lecture room by a model apparatus sent from Christiania.

In the furnaces, as used in Norway, the disc of flame was four or five feet in diameter, and was enclosed in a metal envelope lined with firebrick. Through this furnace air was blown, and emerged charged with nitric oxide fumes. These fumes were collected, allowed time further to oxidize, then absorbed in water-towers or in quicklime—nitric acid and nitrate of lime being the products. The research station near Arendal was described; also the factory at Notodden, in the Hitterdal, where electric power to the extent of 1500 kilowatts was already taken from the Tinnfoss waterfall for the production of nitrate of lime. This product in several forms, including a basic nitrate, was known as Norwegian saltpetre. Experiment had shown that it was equally good as a fertilizer with Chili saltpetre; and the lime in it was of special advantage for certain soils. The yield of product in these furnaces was most satisfactory, and the factory at Notodden—which had been in commercial operation since the spring of 1905—was about to be enlarged; the neighbouring waterfall of Svaelfos being now in course of utilization would furnish 23,000 horse-power. The Norwegian company had further projects in hand for the utilization of three other waterfalls, including the Rjukanfos, the most considerable fall in Telemarken, which would yield over 200,000 horse-power. According to the statement of Professor Otto Witt, the yield of the Birkeland-Eyde furnaces was over 500 kilogrammes of nitric acid per year for every kilowatt of power. The conditions in Norway were exceptionally good for the furnishing of power at exceedingly low rates. Hence the new product could compete with Chili saltpetre on the market, and would become every year more valuable as the demand for nitrates increased, and the natural supplies became exhausted.

[S. P. T.]

Friday, February 16, 1906.

The Right Hon. LORD RAYLEIGH, O.M. M.A. D.C.L. LL.D. Sc.D.,  
President R.S., in the Chair.

W. C. DAMPIER WHETHAM, Esq., M.A. F.R.S., Fellow of Trinity  
College, Cambridge.

*The Passage of Electricity through Liquids.*

OUR subject of this evening owes much of its early development to researches carried on in the Royal Institution. Here Davy investigated the chemical effects of electric currents, and, in 1807, discovered the elements potassium and sodium by the decomposition of the alkalis by the electric current. Here Faraday discovered the quantitative relation between the strength of the electric current on the one hand and the amount of chemical action on the other, and thus raised the subject to the rank of an exact science.

Let us pass an electric current through a solution of some salt, and observe the resultant changes. To make these changes visible, let us choose a coloured salt, such as copper sulphate. As soon as the circuit is completed, we see that one of the copper terminals or electrodes, by which connection is made with the solution, begins to dissolve away, while copper is deposited on the other electrode. Thus copper passes through the solution, disappearing at one end and appearing at the other. The direction in which the copper passes is that which is taken conventionally as the direction of the electric current.

It will be seen that the middle part of the solution is unaffected. The chemical changes occur at the electrodes only; at one copper is deposited, at the other copper is dissolved as sulphate, showing the presence of acid in contact with the metal. The chief facts to be explained then are the appearance of the opposite constituents of the salt—copper and acid—at the electrodes, and the total absence of change in the body of the solution.

We may explain these phenomena by the supposition that oppositely moving streams of the two parts of the salt proceed through the liquid. In the middle there will always be equal quantities of the opposite parts, and the concentration of the solution is unaltered,

but at the ends the parts are set free. The conception may be illustrated by a model, in which differently coloured balls, fixed to movable strings, represent the opposite parts of the salt.

These moving parts of the salt must be electrified, since they move when acted on by an electric force. They were called by Faraday the ions. To a further study of the nature and properties of these ions I ask your attention to-night.

Faraday found that, on passing a steady electric current through a decomposable liquid or electrolyte, the amount of chemical decomposition was proportional to the strength of the electric current, and to the time of current-flow—that is, to the total quantity of electricity which passes. Hence a given quantity of any ion such as copper or chlorine must carry with it a definite charge of electricity. Moreover, the mass of substance deposited by a given current in a given time was found to be proportional to its chemical equivalent weight. Thus equal numbers of equivalents, whether of the same or of different ions, must be associated with equal charges.

If we accept the atomic theory, we must regard the chemical equivalent weight of a substance as proportional to the mass of its atom divided by its valency, i.e. by the number of univalent atoms such as that of hydrogen which one atom of the substance will combine with or displace. Faraday's experiments then mean that each univalent ion carries the same charge of electricity, each divalent ion twice that charge, and so on. The charge on one univalent ion is a true natural unit of electricity, which is thus seen to be quite as atomic in its nature as is matter.

We must now regard the process of electrolysis (i.e. the passage of electricity through a decomposable liquid or electrolyte) as a kind of convection, the electric current being carried through the liquid somewhat as water may be carried from point to point in a number of buckets.

If a current be passed for some time through a solution such as that of copper sulphate, not only is copper dissolved from the anode, or plate by which the current is said conventionally to enter the solution, and deposited at the cathode or plate of exit, but a notable change in concentration is noted in the solution near the two electrodes. The liquid near the anode becomes more concentrated, and that near the cathode more dilute. This may easily be illustrated by an experiment. If instead of copper we use platinum as anode it is not dissolved, and the total amount of copper in solution progressively diminishes. We then find that, while salt is taken from the neighbourhood of both electrodes, more comes from the cathode than from the anode. These phenomena were studied extensively by Hittorf about the years 1850–1860.

Two explanations of this uneven dilution of the solution are possible. We may suppose that the ions are complex structures, and drag unaltered salt or solvent with them through the liquid, or we

may suppose that they move with unequal velocities. It is now probable that in some cases both these factors come into play, but, to simplify our ideas, let us first imagine that the opposite ions are simple, or at all events loaded with equal amounts of salt or solvent, and that they move with unequal speeds through the liquid. The use of the model to which we have already referred enables us to see clearly that the velocity of the anion is to that of the cation as the amount of salt lost by the solution near the cathode is to that near the anode. The ratio of the opposite velocities of simple ions could then be deduced from experiment.

In the year 1879, it was pointed out by F. Kohlrausch that the sum of the opposite ionic velocities might be calculated from a knowledge of the electrical conductivity of the liquid. The conductivity, that is the amount of current conveyed under the influence of a given electromotive force, is obviously proportional to the number of ions, to the velocity with which they move, and to the electric charge carried by each. On the assumption that all the salt is actively concerned in conveying the current, we know the number of gramme equivalents of either ion present from a knowledge of the concentration of the solution. Now Faraday, as we have said, discovered that the amount of substance deposited at the electrodes by a given quantity of electricity was proportional to the chemical equivalent of the substance. This means that a given number of ions, whatever their nature, so long as their chemical valency be the same, carry the same amount of electric charge. The charge on a univalent ion is thus seen to be a true natural unit of electricity; the charge on a divalent ion consists of two such units, that on a trivalent ion, of three. Faraday's quantitative measurements tell us the charge on a gramme-equivalent of any univalent ion. The concentration of our solution tells us the number of gramme-equivalents present; thus, by measuring the conductivity, we can calculate the velocity with which the ions move under a given electric force. By this method, Kohlrausch calculated the specific velocity of many simple ions when moving through dilute aqueous solutions.

In 1886, Sir Oliver Lodge rendered visible the movement of ions which hitherto had been seen by the eye of faith only. By forcing hydrogen ions from a vessel of acid through a tube containing a jelly solution of sodium chloride, he rendered their presence visible by an indicator which changed colour in the presence of an acid, and thus watched their progress through the tube.

In order to compare the ionic velocities as directly observed with those calculated by Kohlrausch, further modifications of the method are necessary. One arrangement which may be used is to employ two solutions which have a common ion, different densities, a nearly equal specific resistance, and different colours. One of these solutions is placed on the top of the other and a current passed across the junction, the movement of which gives us the velocity of the coloured

ions. This method is restricted in scope, but the use of jelly solutions, in which the velocities are not markedly different from those through solutions in water, enables us to use traces of precipitates or indicators to show the movement of various ions. Such experiments showed that the observed velocities were in general agreement with those calculated by Kohlrausch.

If the specific resistances of the two solutions be not equal, interesting phenomena occur at the boundary. The electric force will be greater in the solution where the resistance to be overcome is greater. Hence if an ion from the other solution chance to pass the boundary, it finds itself subjected to a greater force, and its velocity is increased. It will thus be pushed further in advance of the junction if it has got in front, and will be brought up into line again if it has straggled behind. We see, then, that if a junction be advancing in the direction of the solution of higher resistance, the junction will become vague and indistinct, while if the advance be towards the solution of lower resistance the junction will keep sharp and well defined. When the solutions have one ion in common, this means that in order to secure a sharp boundary, we must arrange that a specifically slower ion shall follow a faster one.

Professor Orme Masson recognised that these principles enabled us to dispense with the necessity of choosing two solutions of equal resistance. A salt with quickly-moving ions, such as potassium chloride, is placed in a jelly solution in a horizontal tube. A slow coloured cation is forced electrically into the tube from one end and a slow coloured anion from the other. Thus, blue copper may follow the potassium, and the yellow chromic acid ion  $\text{CrO}_4$  may follow the chlorine. The higher specific resistance in the two coloured solutions forces their ions to conform to the movement of the potassium and chlorine, and thus the motion of the boundaries gives us the velocities of the potassium and chlorine in a solution of constant and known concentration, and therefore their velocities under a known electric force.

Further improvements were made by Mr. B. D. Steele and Mr. F. B. Denison. The use of jelly in the tube was dispensed with by placing membranes over the ends of the tube, and removing them when once the junctions had got well within it. The use of coloured solutions also was found to be unnecessary, for, with sharp junctions, the line of demarcation was visible, owing to the slight difference in the refractive indices of the solutions, and may be shown by projection on a lantern-screen. Denison and Steele have made a careful series of experiments by this method, and, in their hands it is probable that the results thus obtained are more accurate than those given by the methods of Hittorf and Kohlrausch.

The general result of these direct measurements of ionic velocity goes to confirm the indirect calculations of the methods of Hittorf and Kohlrausch, in the case, at all events, of simple univalent ions.



Now Kohlrausch finds that the velocity of any one such ion through a dilute aqueous solution is independent of the nature of the other ion present. Thus, for instance, the velocity of chlorine is the same in dilute solutions of potassium chloride as in solutions of sodium chloride. The velocity under a given electric force is a characteristic property of each ion when moving through a dilute aqueous solution. This result suggests that the ions are independently mobile—that they migrate through the liquid independently of each other.

On this view we must suppose that a large proportion of the whole number of molecules of salt present in a solution is composed of dissociated ions—ions, that is, which are not combined with each other, though they may be linked with solvent molecules. The alternative to this supposition seems to be that the motion of the ions is secured by their passage from molecule to molecule at the instants of inter-molecular collision. On this view, the speed with which the ions worked their way through the solution would depend on the frequency with which collisions occurred. The frequency of collision will depend on the square of the concentration; if the number of molecules be doubled, the number of collisions per second will be four times as great. Hence the velocity of the ions should be greater in concentrated solutions, and the conductivity, which depends on the product of the ionic velocity, and the number of ions, should be proportional to the cube of the concentration. But experiment shows that the velocity of the ions is nearly constant with changing concentration in dilute solutions, and slowly diminishes with increasing strength as the solutions become stronger. We are thus driven back to the idea that the ions migrate independently of each other through the liquid. Much non-electrical evidence pointing to the same conclusion has come to light, and has lent support to the theory of electrolytic dissociation.

I do not propose to enter in this place into a discussion of that theory. But I wish to point out that the evidence, electrical and other, in its favour points merely to a dissociation of the opposite ions from each other; it does not involve the idea of charged particles of, say, potassium or chlorine free from all combination. It may well be that the charged atoms, dissociated from each other, are linked, permanently or temporarily, with one or many molecules of the solvent.

Several facts seem indeed to show that some such combination does occur. If the temperature of a solution be varied it is found that the velocity of the ions alters in about the same ratio as the viscosity of the liquid. Now the viscosity gives the friction which the liquid exerts upon a body moving through it—the dimensions of the body being very large compared with the dimensions of the molecular structure of the liquid. There seems no reason to suppose that the resistance suffered by a single atom, struggling through a crowd of other atoms or molecules, would be related intimately to the

ordinary viscosity. In fact, where the structural dimensions of the medium which determine its viscosity are large compared with those of the moving body, it is known that no such relation holds. Thus there is no proportionality between the variation in viscosity of a salt solution when successive quantities of gelatine are added and the variation in the velocity of the ions of the salt. Here the gelatinous structure is probably a sort of fibrous network, very coarse compared with molecular dimensions.

Thus, the approximate proportionality between variation of viscosity with temperature and variation of ionic velocity, indicates that the dimensions of the ions are probably as large as, or larger than, the dimensions of the molecular structure of the solvent. We may perhaps regard the ions as composed of a central charged nucleus, surrounded by a group of solvent molecules. Such a view is supported by Kohlrausch and by Bousfield.

It should be noticed, however, that the solvent molecules cannot remain attached to the charged nucleus throughout its whole journey. The different ionic velocities of potassium, sodium, and lithium, for instance, indicate differences in the amount of the watery ionic envelope. The amount of water transported through a dilute solution of a chloride by these three ions cannot be the same; it cannot, in each case, be equal to that transported by the chlorine ion. If the water were permanently attached to the nucleus till it reached the electrode, we should get changes in concentration, not contemplated by the theory of Hittorf and Kohlrausch, and the migration constants directly determined by Steele and Denison would not agree with those measured by Hittorf. We must suppose, therefore, that the moving ionic system continually sheds some of its watery envelope, and continually replaces it by fresh water molecules.

One of the most interesting properties of these charged ionic systems is their power of causing the coagulation of certain solutions of colloids, such as albumen. If an electrolyte be added to such a solution in sufficient quantity, coagulation at once ensues, and a curious relation between the coagulative power and the chemical valency of the ionic nucleus enables us to obtain some light on the mechanism of the process. Hardy has shown that colloids themselves generally move through a solution when an electric field is applied, the direction of motion depending on the nature and condition of the liquid solvent. It follows that the colloid particles themselves possess an electric charge, and Hardy finds that the effective ion of the coagulating electrolyte is the ion with an electric charge of sign opposite to that on the colloid. It seems that coagulation is effected by the neutralisation of the charge on the colloid. Now a very much smaller quantity of a divalent salt is able to produce coagulation than is necessary in the case of a univalent salt, and the coagulative power of a trivalent salt is greater again than that of a divalent salt. As mean values, Linder and Picton give for the

coagulative powers of sulphates of univalent, divalent, and trivalent metals the relative numbers 1 : 35 : 1023.

As we saw above, Faraday's experiments show that a univalent ion is associated with one natural unit of electricity, a divalent ion with two such units, and a trivalent ion with three.

Let us suppose that to effect the coagulation of a region of colloid solution, it is necessary for a certain electric charge, equal in amount to that on the colloid particles present and opposite in sign, to be brought within the region. This can only be done by the chance conjunction of ions which, in the absence of an external electric field, must be supposed to be moving in irregular and changeable ways throughout the liquid. If the chance of one ion entering the region be represented by  $1/x$ , that of two ions entering together will be the product of these separate chances or  $1/x^2$ , while the chance of the triple event of these conjunctions will be  $1/x^3$ .

Now, to obtain an equal amount of electricity, we need the presence of 2 trivalent ions, 3 divalent ions, or 6 univalent ions; and, if we work out the problem for solutions containing the same number of molecules, we find that the relative coagulative powers of univalent, divalent, and trivalent solutions should stand to each other in the general approximate ratio of

$$1 : p : p^2$$

The value of the  $p$  depends on unknown quantities, such as the effective radius of ionic action, and cannot, at present, be calculated theoretically. But, by putting  $p$  equal to 32, it is easy to see that the law of increase of coagulative power with valency is that we have deduced; for the theoretical numbers

$$1 : 32 : 1024$$

agree well with Linder and Picton's mean results.

[W. C. D. W.]

Friday, March 30, 1906.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR P. ZEEMAN, *Hon. Mem. R.I.*, of the University,  
Amsterdam.

*Recent Progress in Magneto-Optics.*

IT is my intention this evening to give you a general review of the experimental researches which have occupied me during the last few years. They all refer to the relation between magnetism and light, a relation the first and fundamental example of which was discovered in this very Institution, by Faraday, in 1845.

Surely every physicist should feel inspired by the idea of having the privilege to address an audience in the same lecture room, where so often some of Nature's deeper mysteries were revealed; and I feel the uplifting force of this inspiration all the stronger, as my own work for many years has been so closely connected with one of Faraday's discoveries. Faraday discovered that the plane in which the vibrations of light take place, *rotates* whenever a ray of light is propagated parallel to the magnetic lines of force through some substances, such as Faraday's own heavy glass; this fact we now indicate by the name of the magnetic rotation of the plane of polarisation. The discovery of this fact opened the chapter of magneto-optics.

Faraday's mind again and again returned to the relation between magnetism and light, and incessantly he sought for closer and more intimate connections; in one experiment in March 1862 (which is said to have been his last) he tried to observe a change in the spectrum of a flame, when acted on by a magnet. The entry in Faraday's note book, preserved in this Institution with pious care, concludes with the words, "not the slightest effect on the polarised or unpolarised ray was observed." As we now know, the means of Faraday's time were not powerful enough to observe the effect sought for. Various physicists since Faraday have sought in the same direction; some have recorded their negative results, others have not, for most physicists have an almost invincible dislike for the publication of negative results, though a collection of such unsuccessful attempts, if precisely stated, would be most interesting, and should afterwards prove very valuable.

*Magnetisation of the Spectral Lines.*

In my own case, the thought to submit a source of light to the influence of magnetism occurred to me during a quantitative investigation of the effect discovered by Kerr, concerning the light reflected by magnetised mirrors. I was working at the time in Leiden, in Professor Onnes' laboratory. The account of Faraday's negative experiment encouraged me in my endeavours, and also an argument in 1856 by Lord Kelvin, referred to by Maxwell as the "exceedingly important remark of Sir W. Thomson." If it might be accepted, that the forces operating during the propagation of light in magnetised substances exist also whenever the source of light is in the magnetic field, we can expect some direct effect of magnetism on radiation.

My own successful experiments date from 1896 to 1897, whereas three years earlier I also had recorded a negative result, not having then used adequate means.

As you know, a sodium flame chiefly emits two kinds of yellow light, and accordingly its spectrum when analysed with one of Rowland's large concave gratings, shows two yellow lines. With a grating of medium size, these lines have a distance of one millimetre; they are rather narrow as shown in the slide. In August 1896, I found that when a sodium flame is placed between the poles of an electromagnet, and is looked at with a spectroscope in a direction at right angles to the lines of force, the yellow lines in its spectrum become somewhat wider when the magnetic field is put on.\* This fact can be expressed in a different way by saying that besides the original vibrations, a flame in a magnetic field emits other vibrations, of which some have a somewhat greater, and some a somewhat smaller frequency than the original vibrations.

This observation of a small change in a spectral line was the origin of my subsequent work. I realised that this change, however small, was worth a closer examination. Indeed, it seemed clear at once, that here we had a means of studying the internal vibrations of a molecule by modifying in a simple way the conditions under which they are going on. Of course, the result was verified in all directions. As there is now, I think, no doubt as to the reality of the observed changes, I shall only refer very briefly to this stage of the work. In the first place the widening of the lines was observed in the direction of the lines of force also. Then the fact was established that to the observed *direct* effect, there corresponds an *inverse* one. When white light traverses the incandescent sodium vapour, we observe the absorption lines; these also are widened when the vapour is subjected to magnetic forces. Secondary influences were discarded

\* Zeeman. Verslagen Kon Akademie v Wetenschappen, Amsterdam October and November, 1896. Phil Mag, March, 1897.

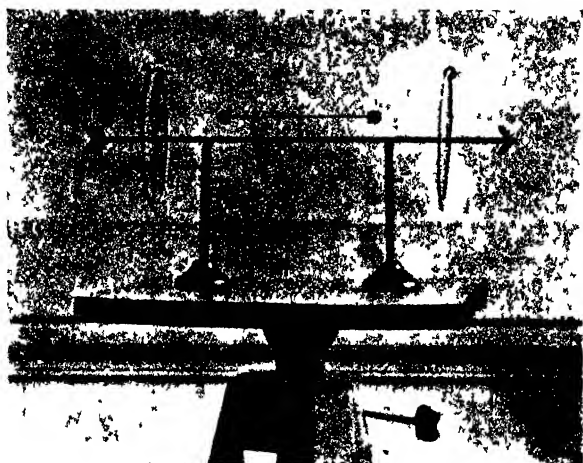


FIG 1

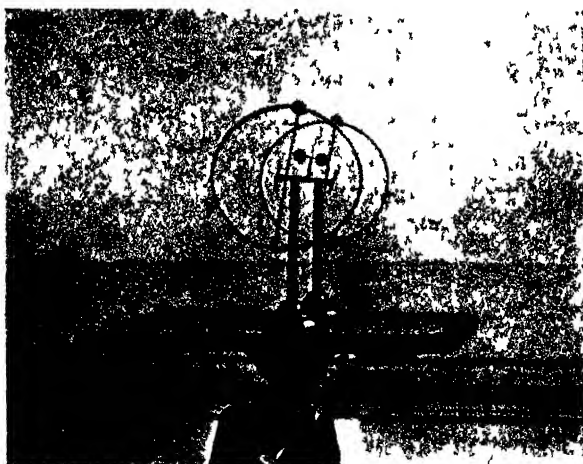


FIG 7

by suitable modifications of the experiments. In one case no change was observed. The spectra of fluted bands, such as those of iodine, carbon, or nitrogen did not show any effect; nor could Becquerel and Deslandres using increased power discover it.

Before I could answer the different questions which presented themselves, I had the advantage that the beautiful theory of the electromagnetic and optical phenomena, developed by my friend Prof. Lorentz, gave its quickening influence on my experimental work.

In this theory, it is supposed that the material world is built up of three things: ponderable matter, ether, and electrons. I think it is rather superfluous to remind you here in the land of Maxwell, Kelvin, Crookes, J. J. Thomson, Schuster, Larmor, Heaviside, and Johnstone Stoney, that electrons or corpuscles are exceedingly small, electrically charged particles, which are supposed to be present in all material bodies.

These electrons can perform oscillations, under the influence of the forces which attract them to their position of equilibrium. Because they are electrified, they have sufficient hold on the ether to excite in it the electromagnetic vibrations, which, according to Maxwell's theory, constitute light.

The oscillatory periods of the electrons determine the position of the lines in the spectrum, and with every change in the period of oscillation we observe a displacement of the corresponding line.

In Lorentz's theory the explanation of the effect of a magnetic field is as simple, as it is beautiful.

The forces operating on the vibrating electron in a magnetic field are fairly well known. These forces are the same which curve the path of the cathode rays in a vacuum tube which is acted on by a magnet. All motions of the electrons in the molecules of a flame may be supposed to be made up of three particular motions, chosen in such a manner that the action of the magnetic field on each of them can be easily foreseen. The light of the flame is exactly the same as it would be, if the flame contained three groups of electrons, vibrating in these simple ways.

In this model, the electrons are represented by red balls, the black arrow indicates the direction of the magnetic force. (Fig. 1.)

As a first simple motion we choose a vibration parallel to the lines of force. On the group of electrons which possess this motion, the magnetic force has no influence; the period, which we call  $T$ , remains unmodified. The other two simple motions are circular motions, clockwise or anti-clockwise, in planes perpendicular to the lines of force.

An electron performing either of these rotations, will be acted on by a force which is directed towards or from the centre, dependent on the direction of the rotation. The magnetic field must, therefore, cause the speed of the electron either to increase or to decrease, and so will either increase or diminish the period. Therefore, instead of one motion with period  $T$ , we get under the influence of the field

three motions with periods  $T$ ,  $T + v$ ,  $T - v$ ,  $v$  being a small quantity. To each motion of the electrons there corresponds a luminous vibration, according to the electromagnetic theory of light. Observing with a spectroscope we must, therefore, see each spectral line divided into three lines; each line becomes a *triplet*.\*

I will show you a few examples of lines which are really divided into three components, in accordance with Lorentz's theory. (Fig. 2, iron; Fig. 3, zinc; Fig. 4, part of iron spectrum; Fig. 5, part of same spectrum.)† You will notice that each of the components remains very narrow; it is not a hazy effect, but a very definite one. This certainly would not be the case if all molecules did not behave in the same manner, and if certain conditions of isotropy of the molecules were not fulfilled.‡

The consideration of the model may illustrate some other points which were foreseen by Lorentz's theory.

Consider the light emitted at a right angle to the lines of force. The three kinds of light seen in this direction are each due to vibrations of one kind, and therefore polarised. We can, therefore, extinguish the light of the central component, or of the two external components of the triplet by a Nicol. In one half of the slide shown, the external components are extinguished; in the other half, the central one. (Fig. 6.)

So, for the first time, we were now able to get polarised radiations from the molecules of a gas. All attempts to produce such simple vibrations from gaseous molecules had hitherto failed.

With some lines, the central component and the outer ones differ much in intensity. If this be the case, the spectroscope can be dispensed with entirely, and we may observe a partial polarisation of the light emitted by the vapour in the field as found by Egoroff and Georgiewsky.

We shall now consider the light emitted in the direction of the lines of force. (Fig. 7.)

It is seen at once that each line must split up into two components. Moreover, both lines must be circularly polarised, but in opposite directions. With suitable arrangements, in one half of the field of view the one, in the other the second component can now be extinguished. I observed this circular polarisation for the first time in the case of the sodium lines now shown. You see how complete

\* Zeeman. Verslagen Kon. Akademie v. Wetenschappen, Amsterdam, Mei, Juni, October, 1897. Phil. Mag., July and September, 1897.

† The photographs illustrating this lecture are, excepting the diagrams, enlarged copies from negatives. The scale is different in the various cases. The separation of the outer components is of the order of one-sixth of the distance of the sodium lines (the vertical lines in Fig. 12). No. 2 is a copy of one of the first photographs I obtained. The author is indebted to Prof. Hunge for Nos. 21, 22, 24. The nonet is not distinctly shown in the latter reproduction.

‡ Lorentz. Annalen der Physik, Bd. 63, p. 278, 1897.





FIG. 2.



FIG. 3.



FIG. 4.

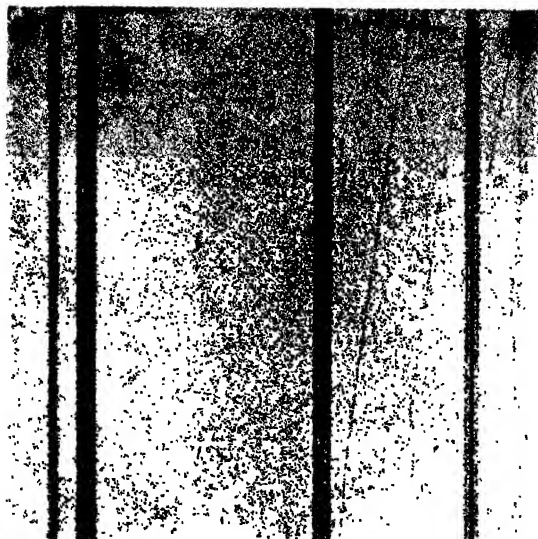


FIG. 5.



FIG. 6.

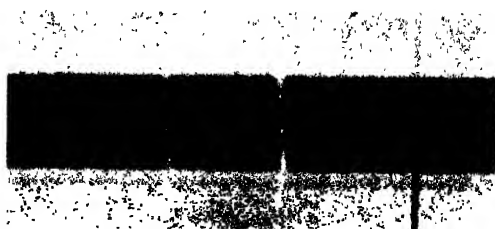


FIG. 8.

the circular polarisation is. There is no trace of rectilinear or of elliptic polarisation.\* (Fig. 8.)

When I first looked for this circular polarisation, I did not have the field of view divided into two parts, but the position of the line was determined by means of a spider's thread. On the reversal of the magnetising current, the luminous line moved. I do not wish to disguise the fact that no observation has ever afforded me so much pleasure as this one.

It has already been remarked that we can also study the absorption lines which become visible when white light is transmitted through the vapour. We then study the inverse effect. I shall use it to show you at least something directly depending upon the effect, because the effect itself is too young to appear before so large an audience. The inverse effect for light parallel to the lines of force plays a part in an experiment due to Righi.† Consider a horizontal ray parallel to the axis of an electromagnet with pierced poles, and let crossed Nicols be placed before and behind the instrument, as in Faraday's experiment. A sodium flame in the field emitting two kinds of circularly polarised rays, absorbs these same radiations, but does not stop the radiations polarised in the opposite direction. These remaining circularly polarised rays cannot be extinguished by a Nicol.

The brilliant yellow spot which appears on the screen as soon as the current is put on, is due to such rays. The explanation of this experiment is not complete however, at least not for denser vapours. The Faraday rotation of the plane of polarisation then plays a part, as we shall see further on.

The magnetisation of the spectral lines allows us to determine whether positive or negative electrons are vibrating in a flame. From the phenomena in the direction of the lines of force, it follows that in a luminous gas the *negative* electrons give rise to all vibrations. It does not follow, however, that the luminous molecules have a negative charge. On the contrary, the researches of Lenard and Stark show that at least part of the luminous spectra is emitted by positively charged atoms.

When a line is split up into a triplet, we can, by measuring the amount of the effect, find out how much matter is loaded with the revolving electron, or in other words, we can determine the ratio of the charge  $e$  to the mass  $m$  of the electron. In this manner, I have made the first determination of this notable number  $\frac{e}{m}$ , and found it of the order of magnitude of  $10^7$  electro-magnetic units per gramme.‡ The most accurate measurements of the present time for different

\* Cf. Larmor. *Aether and Matter*, p. 345, 1900.

† Righi. C.R. 127, p. 216, 1898. C.R. 128, p. 45, 1899. *Nuovo Cim.* (9), 8, p. 102, 1898.

‡ Zeeman. *Verslagen Kon. Akademie*, Amsterdam, November, 1896. § 23.

spectral lines yield values ranging between 1.4 and 1.8 by  $10^7$ . This number is about 1500 times the corresponding number for hydrogen as deduced from the phenomena of electrolysis.

We must, then, conclude that at least a majority of spectral lines is due to the vibrations of the negative electron. This conclusion is not only valid for incandescent sodium or mercury. All elements, which can give colour to a flame, or which can be evaporated in a spark, show the magnetisation of the spectral lines, and hence in all elements these negative electrons are present.

Independent experimental evidence for the existence of electrons has been derived from the study of the cathode rays in a vacuum tube. The discontinuous structure of electricity was also proved by other phenomena, and in this way physicists were led by purely experimental methods to the negatively charged corpuscle of J. J. Thomson, 1500 times smaller than the hydrogen atom, in full accordance with the electron necessitated for the explanation of the magnetisation of the spectral lines.

All fundamental characteristics of the magnetic resolution of the spectral lines were then explained, and the truth of the explanation proved beyond the possibility of doubt. More detailed knowledge of the effect has been greatly extended by a whole series of investigators, especially by Becquerel, Cornu, Cotton, Michelson, König, Righi, Runge and Paschen, and in this country by Gray, Preston, Lodge, Lord Blythwood and others, and from the theoretical side by Larmor, Fitzgerald, Jeans, and J. J. Thomson.

Not all spectral lines are tripled, some are split up into quartets, others into sextets. The lines  $D_1$  and  $D_2$  in strong fields are an example. (Figs. 9 and 10.) The whole of such a system of lines is, even in the strongest fields, confined to the space of one-sixth of the distance of the sodium lines. In some cases still more complicated sub-divisions have been observed, especially by Michelson. In such cases the simple electro-magnetic model of a molecule emitting light is insufficient. We shall return to this subject afterwards, and first proceed to a discussion of *phenomena accompanying the inverse effect*.

This investigation, which I carried out in Amsterdam together with my pupils, Drs. Hallo and Geest, was suggested by a theoretical investigation by Professor Voigt, of Göttingen. Lorentz's theory relates to one single vibrating particle and can only be applied to substances of very small density, which emit very narrow spectral lines. With greater density, and therefore broader spectral lines, the mutual influence of the molecules must be taken into account. It seems, however, that a theory of emission of a system of reciprocally reacting molecules is rather difficult. In the case of absorption the problem is easier and is considered by Professor Voigt, in his theory of magneto-optical phenomena.\* He does not deal with the

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\* Voigt. *Annalen der Physik*, Bd. 67, S. 345, 1899.

Fig. 11

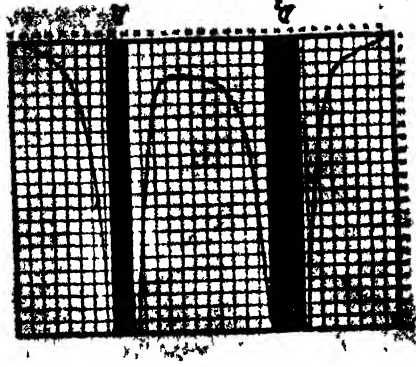


Fig. 9.

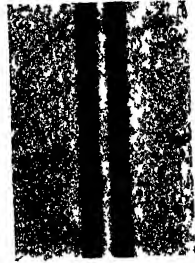


Fig. 10



electrons directly, but adds suitable new terms to the equations of motion in an absorbing medium. His method establishes a connection between the rotation of the plane of polarisation and the resolution of the spectral lines, a connection almost simultaneously pointed out by Fitzgerald. This also led to an interesting result, till then missed by the electronic theory, namely :—

*Rotation of the Plane of Polarisation close to an  
Absorption Band.\**

Faraday's rotation of the plane of polarisation is extremely small in all gases, also in sodium vapour. Only within a very narrow range close to the sodium lines the rotation is positive and very great, a fact discovered by Macaluso and Corbino. In a recent extremely interesting paper, Professor Wood has given measurements of observed rotation of four complete revolutions.† This, however, was in rather dense vapour, at least dense in comparison with the vapour used in the experiments now to be described, in which vapour containing about one-millionth gram of sodium per cm.<sup>3</sup> was used.

The magnitude of the rotation close to the sodium lines is illustrated by measurements made by Dr. Hallo in the Amsterdam laboratory. It is clear that on both sides of an absorption line the rotation is in the same direction. (Fig. 11.)

We may attenuate the vapour still further so that the doublet in the direction of the lines of force becomes visible. What is the rotation then between the components of the doublet?

It is easily deduced from Professor Voigt's theory that, in very diluted vapours the rotation must occur, in a sense, opposite to that outside the components, and therefore negatively, and also that it must be very great. In the case of sodium vapour, I had the pleasure to confirm this theoretical result, and to observe rotations of  $-400^\circ$ .

In these experiments interference fringes in the spectrum were used, established by means of a system of Fresnel quartz wedges (a method used by Voigt, Corbino, and others in similar cases). I will project these fringes on the screen.

If a plate of quartz, which rotates the plane of polarisation, is held in the ray, you will notice a displacement of the fringes. A plate of glass has no influence of course. I have here a quartz plate which rotates the plane of polarisation through  $90^\circ$ , and you will notice a displacement of half the distance between two fringes. A displacement of the entire distance between two fringes corresponds to a rotation of half a revolution.

\* Zeeman. Proc. Ac. Sciences, Amsterdam, May, 1902. Hallo. Thesis, Amsterdam, 1902, Archiv, Néerl., ser 2, T. 10, p. 148, 1905.

† Wood. Phil. Mag., October, 1905.

Analysing the light by means of a Rowland grating we can produce such a system of fringes for all wave-lengths, and we can consider the rotation for wave-lengths close to the controlling absorption bands. On the screen I will first project the fringes close to the sodium lines with the field off. The dark vertical lines are the sodium lines. They are broad, because the vapour is rather dense. The horizontal bands are the interference fringes. (Fig. 12.)

With the magnetic field on, the image now projected is seen. (Fig. 13.)

You see how fast the rotation increases in the vicinity of the absorption lines, becoming more than  $180^\circ$  closer to the bands. In the interior of the bands only a hazy fringe is seen. A remarkable equation, first deduced by Becquerel,\* gives the law of the rotation.

The phenomenon is more beautiful as soon as the vapour is so thin that the doublet is seen. (Fig. 14.)

Outside the components of the doublet the fringe rises *upwards*. But inside the components the fringe has moved *downwards*, the rotation is negative there. The rotation is  $-90^\circ$  for  $D_1$ , nearly  $-180^\circ$  for  $D_2$ . It is very interesting to watch the movement of the fringes in the spectroscope as the field is increased or the density of the vapour changed.

### *Double Refraction and Resolution of the Absorption Lines.*

In the second place we will now consider the *double refraction* which occurs whenever light traverses a vapour at right angles to the magnetic field. A plane wave with vibrations parallel to the field has a velocity different from that of a wave with vibrations at right angles to the field. It is only close to the absorption band that the difference becomes perceptible. Sodium vapour in a magnetic field behaves as a double refracting crystal for light close to the sodium lines. This result of Voigt's theory was verified by him in conjunction with Wiechert in the case of dense vapours, and commented upon by Becquerel and Cotton.

With great density, and using the same system of interference bands, the phenomenon assumes the appearance now projected. Whereas the rotation of the plane of polarisation was symmetrical on both sides of the absorption band, you see that the double refraction is not. On one side of the absorption line, sodium vapour behaves like a positive crystal, on the other side like a negative one.

With very dilute sodium vapour, and with a magnetic field strong enough to resolve the sodium lines, the theory must be extended. There is no difficulty here.

The observations made by Mr. Geest, as well as by myself, con-

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\* Becquerel. O.R. 125, p. 679, 1897. Cf. also Schuster. *The Theory of Optics*, p. 291-294, 1904. Siertsema. *Proc. Ak., Amsterdam*, 12, p. 499, 1903.

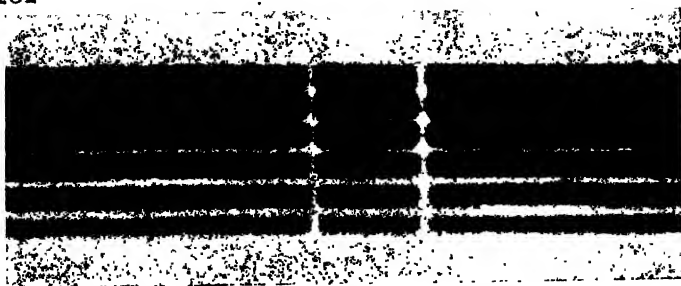


FIG. 12.

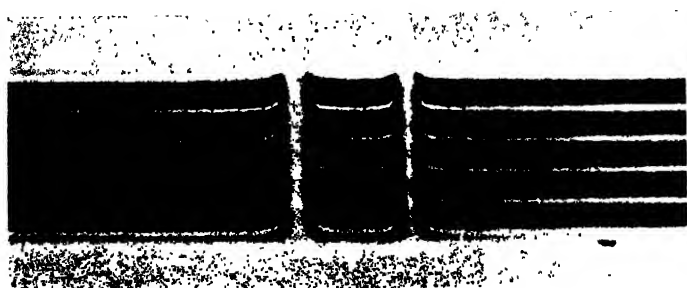


FIG. 13.



FIG. 14



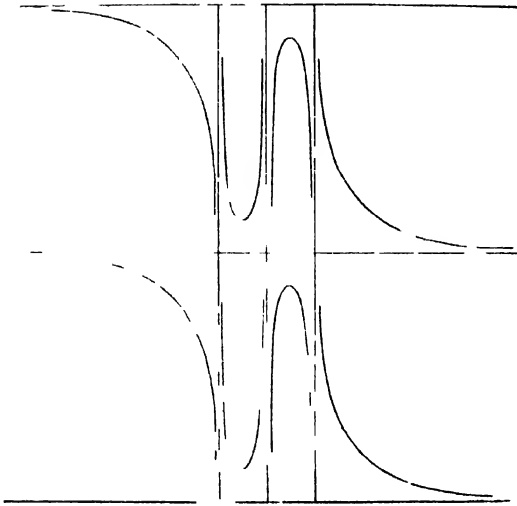


FIG 15



FIG 16.

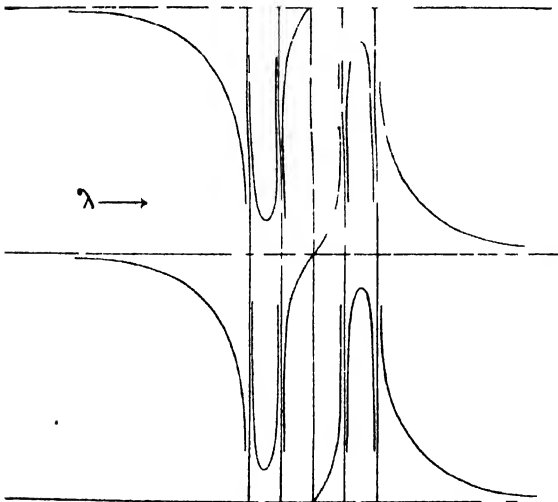


FIG. 17



FIG 18.

cerning the details of this double refraction, have fully confirmed Voigt's theory.\*

The slides shown always refer to *one* of the yellow sodium lines, and hence the structure seen is almost entirely confined to the extremely small region between the components of one line.

The line  $D_1$  splits up into three components in a moderate field. The theoretical course of double refraction is given in a diagram; next to it the result of observations is given. (Figs. 15 and 16.)

On a somewhat larger scale the appearance is as now shown; with greater density the characteristic sinuous line undergoes transformation.

The line  $D_1$  splits up into a quartet. Besides the concave parts you will now notice a line with a point of inflexion in the theoretical and in the observed curves. (Figs. 17 and 18.)

The same phenomenon is again illustrated by the next slide, where also the change which occurs with greater density is manifest. In a very strong field the line  $D_2$  is resolved into a sextet. The inverse sextet can be readily seen with the means at our disposal. But the phenomena occurring between these narrow spaced components could only be seen with difficulty. Only under very favourable circumstances Mr. Geest observed the image now projected.

All the described phenomena are qualitatively in excellent accordance with Voigt's theory. It is certainly very interesting that the theory is able to explain the complicated course of double refraction by the difference between the velocities of propagation of vibrations at right angles and parallel to the field.

### *Magnetic Resolution and Intensity of Field.*

Let me again refer to our first subject, the magnetic separation of the lines. The magnitude of this separation is proportional to the intensity of the field in which the source is placed. We may, therefore, deduce the intensity of the field from the magnitude of the magnetic separation. We have only to measure the distance of the components of a suitable line. It is not generally known that this distance can be increased with great accuracy (with an error of far less than 1 per cent.). It is, therefore, far easier, if a relatively high degree of accuracy is necessary, to compare the intensities of field by measurements of the distance between the components than by direct magnetic measurements.

All methods used for the measurement of magnetic fields give us the intensity in a point. On the other hand, the magnetic resolution of spectroscopic lines can give us the intensity in *all points belonging*

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\* Zeeman and Geest. Proc. Acad. of Sciences, Amsterdam, May, 1903, December, 1904. Geest. Thesis, Amsterdam, 1904, Archiv. Néerl, sér 2, T. 10, p. 291, 1905.

to a line. Moreover, in this manner, we make direct use of a property of the atom.

You see here a vacuum tube with some mercury. We heat the tube and excite it with the coil. You notice the brilliant light which is, however, greatly increased when the tube is placed in a magnetic field.\*

For a given density of the vapour, there is a definite intensity of field for which the luminosity is a maximum. You can see this when we put on the current in the electro-magnet, the intensity of the field then rises gradually.

We project an image of the tube on the slit of a spectroscope. This spectroscope must be so arranged that to every point of the slit there corresponds a point of the image. The blue line of mercury (4359) resolves into a sextet. Using this line the field of a du Bois electro-magnet with a pole distance of 4 mm. is mapped out in the spindle-shaped optical magneto-grams now shown. (Fig. 19.) We may, of course, extinguish the light of the inner components. In some cases a triplet will give more accurate results. The method sketched will, of course, only be applied in difficult cases. As long as our spectroscopes of great resolving power are rather cumbersome, there is no practical application for the method.

By means of this method we may also study some questions as to the way in which certain phenomena, which accompany the resolution, depend on intensity of field.

We have no time, however, to discuss this further, because I should like to refer to the important subject of the

### *Behaviour of the Different Lines in the Magnetic Field.*

In many metallic spectra a number of lines occur which are closely related and form so-called series of lines. The important discoveries of Hartley, Liveing and Dewar were followed by the discovery of series, owing to the indefatigable efforts of Balmer, Kayser and Runge, Rydberg and Schuster.

The plate shows diagrammatically the arrangement of the three connected series which are found in the spectra of the alkalis and other elements, and which are distinguished by Professor Schuster † as the trunk series (Kayser and Runge's "Hauptserie"), the main branch series (Kayser and Runge's "Zweite Nebenserie"), and the side branch series (Kayser and Runge's "Erste Nebenserie").

The laws of these series are simpler than those governing acoustical vibrations. They are of an entirely different character; for instance, the members of each series approach some definite limit of frequency, whereas the number of acoustical vibrations may increase indefinitely.

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\* Paschen. Physik. Zeitschr., I. S., 478, 1900.

† Schuster. The Theory of Optics, p. 282, 1904.



FIG. 19

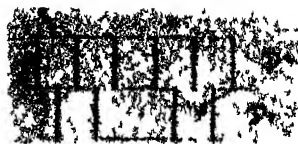


FIG. 20



FIG. 21



FIG. 22.



FIG 23



FIG 25



FIG 24

My first measurements already made it evident that lines of different series behaved entirely unlike each other.\* Hence the ratio of charge to mass could not be the same for all vibrating electrons.

Runge and Paschen have proved in a most beautiful and systematic investigation † that all the lines of a trunk or of a branch behave in the same manner. This result was first announced by Thomas Preston,‡ but it is not stated to what degree of accuracy and for how many lines he investigated the subject.

All lines of the same series are split up in the same manner, e.g. all lines are resolved into triplets or all into nonets. Moreover, not only the general type of sub-division is the same, but even the amount of separation, when measured in oscillation frequency.

The second law discovered by these physicists is this: That corresponding series of *different* elements show the same type of resolution, and the amount of separation is the same when measured on the frequency scale.

In the alkalis, each line of the trunk series is double, and we may speak of a twin trunk. The yellow sodium lines are a typical example. The type of resolution of the two lines is shown in the diagram. (Fig. 20.) Here we have again our old sodium lines in the field. The same division occurs in all cases when twin trunks exist. Substances so different in chemical behaviour as sodium, copper, silver, and calcium (e.g. the well known lines H and K), split up in the same manner. And I think that even Sir William Crookes will be surprised to hear that his thallium lines are in the magnetic field only counterfeit sodium lines. I can show you the splitting up of these beautiful thallium lines in the slide. (Figs. 21 and 22.)

With zinc, cadmium, mercury, calcium, there are *three* main branches associated with each other. The amount of separation is the same in each of these branches. The type of resolution is shown in the diagram. (Fig. 23.) I can show you further lines of mercury, the triplet, the sextet, the nonet. Another example of the same sextet is given by a zinc line. The next slide refers to some beautiful magnesium lines, exhibiting the same three types of resolution. (Fig. 24.)

We see that in these cases the simple image of an oscillating electron does not apply. I regret to say that the electronic theory cannot yet give us the explanation of the more complicated resolutions, even for the quartet, we are yet in want of a model.

\* Zeeman. Verslagen Ak. v. Wetenschappen, Amsterdam, December, 1897. Phil. Mag., February, 1898.

† Runge and Paschen. Berl. Akad. Abhandlungen, Anhang, 1902. Sitzberichte, Berlin, p. 880, p. 720, 1902. Runge. Physik Zeitschr., 8. Jahrgang, S. 441. Kayser. Spektroskopie. Band 2. Kapitel IX., 1902.

‡ Preston. Dublin Trans. (2) 7. p. 7-22, 1899.

The laws discovered, however, seem to point to the conclusion that all the lines of a series are emitted by one oscillating system, that there are, therefore, as many series in the spectrum of a substance as oscillating systems in its atom; moreover, that the oscillating mechanism is the same in different elements. We are reminded here of the view advocated by Sir Norman Lockyer that the different elements have something in common.

The relation between these spectral series and resolution in the magnetic field is so close that we may expect that the solution of the problem of the series will give at the same time the solution of the magnetic separation problem.

That Lorentz's theory is on the right track even in the case of the more complicated magnetic effects appears from the polarisation of the nonet shown in the slide. (Fig. 25.)

Three groups of vibrating lines here correspond to the three lines of the triplet.

The circular polarisation corresponds also to that of the doublet indicating that it is always the negative electron which executes the vibrations.

There is y<sup>et</sup> room enough for experimental work in extending these investigations in different directions and to other elements.

Much light on our present subject will be thrown undoubtedly by the activity in adjacent chapters of physics. I can only mention in this relation the extremely interesting experiments by Lenard and Stark on the centres of emission of different spectral series, and the important theoretical work by Drude\* on the optical properties and electronic theory.

Maxwell has said "an intelligent student armed with the calculus and the spectroscope can hardly fail to discover some important fact about the interior structure of a molecule." I think this statement remains as true now as it was thirty-two years ago.

There can be no doubt, I think, that spectrum analysis and especially the magnetisation of the spectral lines will give us a clue to the inner structure of the atom.

I hope that I have succeeded in imparting to you this, my conviction.

[P. Z.]

\* Drude. *Annalen der Physik*, pp. 677, 936. Bd. 14, 1904.

Friday, June 8, 1906.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. P.C. D.C.L.  
F.R.S., President, in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,  
Fullerian Professor of Chemistry *R.I.*

*Studies on Charcoal and Liquid Air.*

THE object of the lecture was to demonstrate experimentally a few novel applications of liquid air observed in the course of laboratory experiments. Some of them may be said to take the character of lecture illustrations, while others deal with an extension of the scientific uses of charcoal at low temperatures, a subject which was first discussed in a Friday Evening Discourse delivered by the Professor in the year 1896.

*Electrical Stimulation at Low Temperatures.*

Bodies cooled to the temperature of liquid air have the surface film of water, which is more or less deposited on them, frozen exceptionally hard, and therefore not in a good condition for the dissipation of any electric charge that may be given to them. The result is that a substance like glass cooled in liquid air is exceedingly easily electrified by friction, and retains its charge for a long time. This property of glass was shown in the following manner :—

A glass tube shaped like a two-pronged fork was arranged so that a magnified image of it could be projected on a screen. (See Fig. 1.) The prongs were cooled in liquid air, and one prong, A, while it was being removed from the liquid air, was gently flicked with flannel or silk to electrify it. On being exposed to the air the moisture in the atmosphere was deposited as ice on both prongs, but the character of the deposit was different on the unelectrified and the electrified prong, crystals of ice beginning to form on the latter, speedily causing it to assume the appearance of a miniature forest of growing and moving crystals shown on A in Fig. 1, while B shows simply a dead coating of ice. The electrified prong by induction attracts the moisture in the air, and as fresh moisture is drawn in repulsion between like electricities causes the new crystals to be deposited as far out as possible, thus presenting the appearance in the diagram. With good projection one can see some of the crystals on A repelled and shot across to B. A similar experiment



of another kind is the facility with which an electrified glass rod clears up ordinary opalescent liquid air by attaching the finely suspended impurities of ice crystals, solid carbonic acid, and organic matter to its surface when moved about in the liquid. The same thing may also be done by moving about a crystal of nitrate of uranium, which by cooling becomes highly electrified without the need of direct friction as when glass is used.

*The Spheroidal State of Liquid Air on the Surface of Liquids.*

As volatility depends on vapour pressure, of two liquids that having the higher vapour pressure at any given temperature is necessarily the more volatile. The difference in the facility of condensation of the vapours produced by different liquids may easily be demonstrated by the use of liquid air.

A series of liquids with different boiling points, like : tetrachloride of carbon ; water ; caustic potash solution ; benzoic ether ; and strong sulphuric acid ; were selected, and each placed to the depth of about an inch in a number of shallow cylindrical cups, as shown in Fig. 2, the surfaces of which could in succession be projected on a screen by means of a horizontal lantern.

On allowing drops of liquid air to fall on the surfaces of these liquids, best by filtration through a small filter-paper funnel, they immediately assume the spheroidal state, and the projection through the liquid showed they were moving about with considerable rapidity, impinging on the sides of the vessel and getting deflected like an elastic body, while followed by clouds of condensed vapour, the relative amount of which may be taken as roughly proportional to the volatility of the liquid. With water the cloud was very dense, being less so in the case of the alkali solution, more so for the tetrachloride of carbon and least for sulphuric acid. On the sulphuric acid the drops moved about slowly owing to the high viscosity of the liquid, but with hardly any cloud, while on the surface of benzoic ester, a lively agitation accompanied by a light cloud was observed. In the case of the tetrachloride of carbon, the effect was most striking : dense clouds swayed to and fro over the surface, and the drops of liquid air shot to the walls of the vessel at all angles of incidence and rebounded, followed by tails of vapour, making them look like miniature comets. In order to secure a good view of the movements, it is necessary occasionally to blow the fume away from the upper part of the vessel by a current of dry air. Care must be taken to avoid the fall of too much liquid air in one place, which would cause a rapid local cooling of the liquid attended with solidification, which inevitably arrests all spheroidal motion. This may be prevented to a great extent by having the liquids in the vessels used for projection slightly heated before the experiments are begun.

FIG. 1.

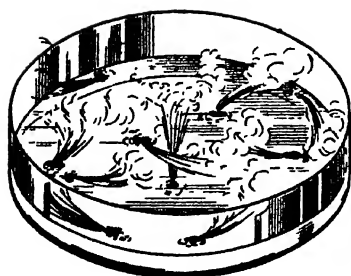
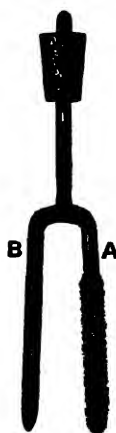


FIG. 2.

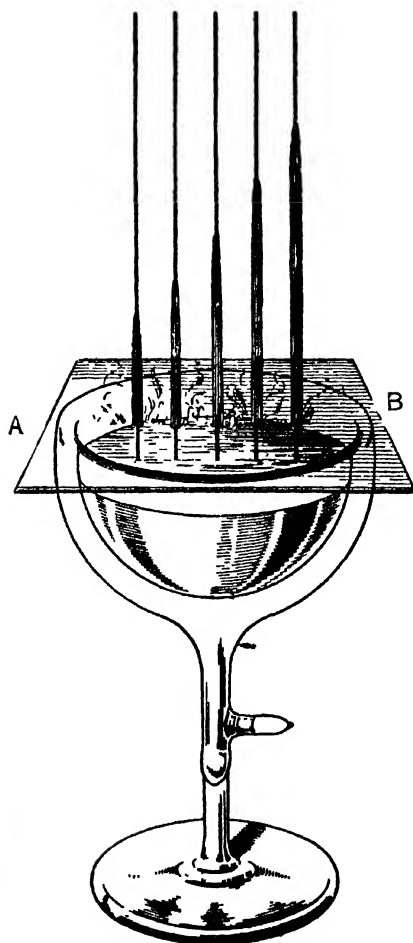


FIG. 3

*Thermal Conductivity.*

Going to another subject, the well-known experiment of Ingenhousz on the relative conductivities of metals may be repeated at low temperatures by means of liquid air.

A vacuum-jacketed cup V (see Fig. 3) is filled with liquid air and covered with a sheet of mica (A B), having a set of small holes in it, through which a series of equal wires of different metals (copper, brass, bismuth, etc.) are fixed. After immersing their lower ends in the liquid air a coating of frozen moisture is deposited from the surrounding atmosphere, and is seen to collect round the lower parts of the wires above the mica screen, ultimately forming definite heights of an ice cap on each wire according to their conductivities. As in the Ingenhousz experiment, the relative conductivities are proportional to the squares of the heights to which the ice ultimately rises on the wires above the level of the mica sheet. In this manner it is possible to determine rapidly conductivities at low temperatures. The following table gives some rough measurements made in this way:—

	Bismuth.	Fusible Metal	Lead.	German Silver.	Tin	Steel	Iron	Brass	Copper.
Height of ice in mm.	10	27	38	40	54	57	62	65	145
Conductivities — copper being taken as 1.	·005	·035	·069	·076	·139	·155	·183	·201	1·000

A similar method might be employed to determine conductivities at temperatures lower than the melting point of ice; for instance, the experiment might be made in a dry hydrogen atmosphere containing a small amount of sulphurous acid, continuously renewed, in which case the relative conductivities would be found from the melting point of sulphurous acid instead of from that of ice.

*Gas Absorption by Charcoal at Low Temperatures.*

Some of the more important facts regarding the absorption of gases by charcoal at low temperatures were detailed in the address given in 1905, entitled "New Low Temperature Phenomena," and to those a few additions were made due to further experience. Other porous materials are found to possess the power of absorption for gases at low temperatures to a less extent. Thus dry aluminium oxide shows a remarkable power of absorbing air just like charcoal, one gramme condensing at atmospheric pressure some 70 c.c., and the

same property is possessed by meerschaum and silica. The retentive power of alumina is much inferior, however, to that of charcoal, and consequently is of no use in forming high vacua. All charcoals possess the property of gas absorption at low temperatures. Light charcoal, such as is used in the manufacture of gunpowder, or the variety got from animal substances like blood, both act, but experiments made at the Royal Institution show that charcoal prepared by careful carbonisation from cocoa-nut is one of the most convenient varieties to use. While using the same process of carbonisation, the absorptive effect is enhanced by making it take place slowly and with gradually increasing temperature. With the samples made a year ago, it was possible to get an absorption of about 150 c.c. of air per gramme of charcoal at  $-185^{\circ}\text{C.}$ , but with care the amount can be raised to as much as 350 to 400 c.c. per gramme.

The amount absorbed at atmospheric pressure and at the temperature of liquid air can be quickly determined. A gramme of charcoal, previously heated to a red heat is placed in a glass bulb connected by an india-rubber tube and stop-cock to a graduated vessel containing air kept over strong sulphuric acid or a high boiling point oil, so that on cooling the charcoal and opening the stop-cock the absorption is measured. This absorptive power can be shown by means of the balance and the electro-magnet. From one arm of a balance was suspended a copper-wire gauze sphere containing charcoal which was carefully counterpoised. A flask partly filled with liquid air was now brought up below it, so that the vapour rising from the liquid air surrounded the charcoal. The absorption soon became visible through the beam of the balance descending as the charcoal became charged, and by adding weights the amount of gas absorbed per unit of time could be determined. If a rod of charcoal was hung up by a thread between the poles of an electro-magnet and sufficient torsion applied, so that its length was at right angles to the line joining the poles, when the magnetic field was produced, on bringing a vessel of liquid air close below it after a short time on turning on the electric current to "make" the magnet, the rod now set itself along the line joining the poles, proving that it had become magnetic. This action is dependent on the well-known magnetic property of oxygen, one of the constituents of the air, which surrounded the charcoal rod and which had condensed within its pores. On taking away the cool vapour of the liquid air the temperature soon rose and the behaviour of the rod under magnetic action showed that it had lost the magnetic property.

*Effect of Increased-Pressure of Gas on the Absorption of Charcoal at Low Temperatures.*

The absorption of hydrogen by charcoal at the temperature of liquid air and under atmospheric pressure is very considerable, and

the question arises how much more could be got in by the use of higher pressure. The amounts absorbed by 6.7 grammes of charcoal, at the temperature  $-185^{\circ}\text{C}$ . for various pressures are given in the following table :—

Pressure in Atmospheres.							Volume in Cubic Centimetres.
1	..	..	..	..	..	..	620
5	..	..	..	..	..	..	925
10	..	..	..	..	..	..	1,050
15	..	..	..	..	..	..	1,000
20	..	..	..	..	..	..	975
25	..	..	..	..	..	..	925

The amount absorbed is seen to increase with the pressure to 10 atmospheres, after which the absorption in the pores of the charcoal seems to be independent of the pressure. At the temperature of liquid air this sample of charcoal would not absorb more than one litre of hydrogen, even when the pressure was raised from 10 to 25 atmospheres or the absorption had come to a limit. Increased absorption, which does not reach more than twice that at the ordinary atmospheric pressure, is the sole result of the use of higher pressures.

*Vacua produced by Charcoal under different circumstances.*

The absorptive power of charcoal for air is very remarkable. On stopping the passage of a stream of air into a charcoal bulb immersed in liquid air, to which a small manometer was attached, hardly any gas pressure was shown. This was further exemplified by the action of a Röntgen tube, partially exhausted, connected to a charcoal bulb. On immersing the bulb in liquid air the characteristic phosphorescent glow of the Röntgen tube was soon reached, but disappeared when the liquid air was removed. When hydrogen was used instead of liquid air, the pressure was so much reduced that the glow was entirely stopped. A Crookes's radiometer, filled with hydrogen at atmospheric pressure, had a charcoal bulb attached. On immersing the charcoal bulb in liquid air no rotation took place, even when the beam of an electric lamp was thrown upon it; but when liquid hydrogen replaced the liquid air the motion became exceedingly rapid. This shows that high vacua can be attained by the use of charcoal in an atmosphere of pure hydrogen, provided it is cooled in a liquid hydrogen bath instead of liquid air. A similar radiometer, filled with helium at atmospheric pressure, remains inactive even when liquid hydrogen is the cooling agent, thus proving that the absorption of the helium by charcoal at  $20^{\circ}\text{abs}$ . is relatively inefficient for the production of vacua as compared with hydrogen. This is only another mode of proving the much greater volatility of helium over hydrogen.

*Laws of Absorption at Low Temperatures.*

The general laws of the dependence of the absorptive power of charcoal upon the pressure, temperature, and volume of the gas absorbed are apparently complicated, but in average circumstances they can be stated approximately. For a supply of gas at constant pressure the volume and temperature are related by a curve of hyperbolic form. There must clearly be a lower limit of temperature for absorption, for the gas will eventually liquefy; on the other hand, however small the absorption may be, as the temperature rises it can never entirely vanish. If the temperature be kept constant we should expect an increased absorption with increasing pressure up to a certain limit. Experiment indicates that this is the case, and we have again a curve of hyperbolic form connecting pressure and volume, but differing from the previous case in having the convexity turned the opposite way. When the pressure is small the absorption will be a minimum, but any slight increase of pressure will be associated with the molecular attraction of the charcoal, and the absorption may be expected to increase much more rapidly in proportion to the pressure. Finally, when the volume absorbed is kept constant the relation between the pressure and the temperature is of a logarithmic form, like those of a saturated vapour or a dissociating body.

For the absorption of hydrogen in charcoal at the temperature of liquid air the expression  $\log p = a + bV - cV^2$  holds, where  $p$  is pressure,  $V$  the volume of gas occluded, and  $a$ ,  $b$ , and  $c$  constants. For small concentrations of gas the pressure grows in a linear relation to the volume.

*Hypothetical Densities of Gases Occluded in Charcoal.*

Mitscherlich's measurements made on the charcoals used by him showed that in a piece of charcoal the space occupied by charcoal-substance is to the pore-space nearly in the ratio of 13 to 20. The Professor's observations on the real and apparent densities of cocoanut charcoal lead to the conclusion that in 100 grammes the pore-space may be taken on the average as about 15 c.c. This enables us to compare the average hypothetical density of any absorbed gas with the density of the same gas when liquefied. The following table shows some such comparisons, and it may be noted that the densities of the absorbed gases at their boiling-points are equal to or a little greater than the corresponding liquefied gases at the same temperatures, so far as they are known. Whether the density of the monadic gases will turn out as satisfactory is a matter for future inquiry.

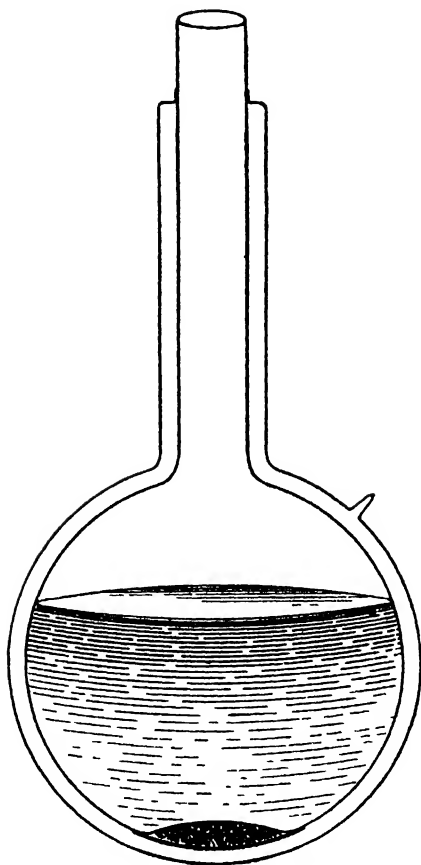


FIG. 4.

Gas.	Temperature of Absorption.		Density of Gas Occluded in Charcoal.	Density of Gas Liquefied
	Cent.	Abs.		
Carbonic acid . . . .	+ 15°	288°	0·7	0·8
Oxygen . . . . .	— 183°	90°	1·33	1·12
Nitrogen . . . . .	— 193°	80°	1·00	0·84
Electrolytic gas . . . .	..	..	0·58	?
Hydrogen . . . . .	— 193°	80°	0·06	0·07
“ . . . . .	— 210°	63°	0·08	..
“ . . . . .	— 252°	21°	0·11	..
Helium. . . . .	— 258°	15°	0·17	?

### *Metallic Vacuum Vessels.*

With the aid of charcoal, it is easy to make useful vacuum vessels of metal instead of glass. The metallic vessels resemble the ordinary glass silvered vessels and are of from 2 to 10 litres capacity (see Fig. 4). The envelopes may be made of brass, copper, nickel, or tinned iron, with necks made of a bad conducting alloy. The vacuum between the walls of these vessels was maintained by enclosing some charcoal in a small globular space, A, constituting part of the inner vessel that is filled with liquid air. The necks may be covered with silvered glass vacuum cylinders which act as stoppers, and at the same time utilise the cold of the slowly evaporating liquid. The efficiency of the best metallic flasks is equal to that of the chemically silvered glass vacuum vessels, now generally used in low temperature investigation. Vessels of this type will be of use in industrial cryogenic operations and for the storage and safe transit of liquid air.

### *Diffusion of Gases into Charcoal at Low Temperatures.*

Although, as regards general absorption, charcoal under corresponding conditions behaves in a similar manner to all gases, nevertheless it possesses a certain selective power, when in presence of a mixture of gases. A quantity of charcoal which has been heated, exhausted, and then saturated with ordinary air at  $-185^{\circ}\text{C}$ ., must have gases occluded in its pores of the average composition of the air. Let, however, a stream of air at the same low temperature pass slowly and continuously over it for some hours, and it will be found that at first the issuing gas is almost pure nitrogen, while the occluded gas reaches a new and definite composition. If now the gas absorbed by the



charcoal be expelled by heating it to the ordinary temperature, it will contain on the average some 60 per cent. of oxygen. Fig. 5 represents roughly the molecular composition of the air initially present in the pores of the charcoal, namely, about four molecules of nitrogen to one of oxygen. The final average molecular composition of the absorbed gas after the passing of the slow current of air, cooled to  $-185^{\circ}\text{C}.$ , over the charcoal is similarly represented in Fig. 6, where it can be seen that diffusion, or fractional distillation at constant temperature, has gone on until about two of the molecules of nitrogen have been replaced by two of oxygen. If the charcoal, in equilibrium with air gases in the condition specified in Fig. 6, has a current of hydrogen at the temperature of liquid air passed over it, the hydrogen will diffuse in, until about one molecule in five is present, as shown in Fig. 7. Again, if charcoal be saturated with oxygen to begin with, and hydrogen be passed over it when cooled to  $-185^{\circ}\text{C}.$ , the hydrogen will diffuse in, until it constitutes one-third of the gas present in the pores (Figs. 8 and 9). Similarly, if we employ nitrogen in place of oxygen, the hydrogen will displace about two-thirds of the nitrogen (Figs. 10 and 11). On the other hand, if the charcoal be initially saturated with hydrogen at  $-185^{\circ}\text{C}.$  (Fig. 12), and air passed over it at that temperature, the whole of the hydrogen is practically displaced, and the gas remaining in the charcoal is represented by the composition shown in Fig. 13, which is the same as in Fig. 6.

If, instead of analysing the whole of the occluded gas that is given off, samples are taken from the charcoal between definite temperatures, from the boiling point of air up to the ordinary temperature, then a regular fractionation of the occluded gases takes place, resembling that of an ordinary mixed liquid, and the problem is an entirely different one. Further, even in the simpler mode of treatment as described above, the relative proportions of the absorbed gases depends at any time after the experiment has started upon the relation between the current of gas used at the constant temperature of  $-185^{\circ}\text{C}.$ , and the nature and condition of the charcoal. The simplification of the problem is due to making the time very long.

#### *Chemical Interactions at High Vacua.*

If a piece of pure sulphur (S) is put in one end and some mercury (Hg) in the other end of a U-tube (Fig. 14), both substances being kept at the temperature of liquid air during the time required to reach a high vacuum by the mercurial pump or by charcoal exhaustion, and the whole sealed off and left to stand at the ordinary temperature; then in a few hours, it will be noted that the surface of the mercury which was at first a brilliant reflecting one gets tarnished from the formation of a film of sulphide of mercury. The mercury vapour pressure being much greater than that of sulphur, it would be expected that any formation of sulphide of mercury taking place

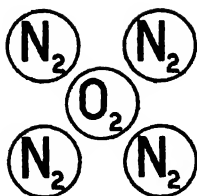


FIG. 5.

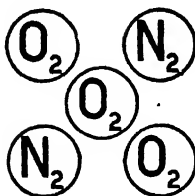


FIG. 6.

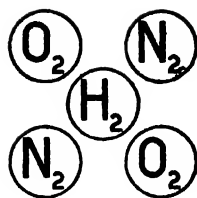


FIG. 7.

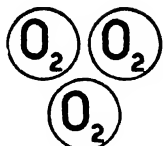


FIG. 8.

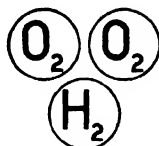


FIG. 9.

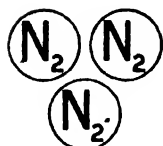


FIG. 10.

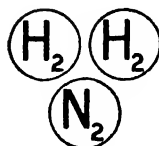


FIG. 11.

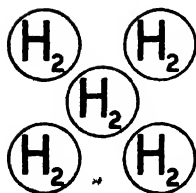


FIG. 12.

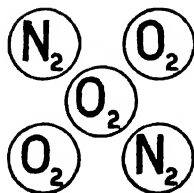


FIG. 13.

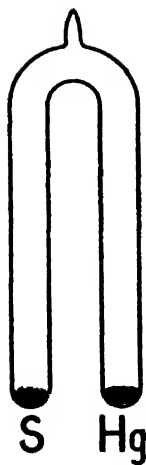


FIG. 14

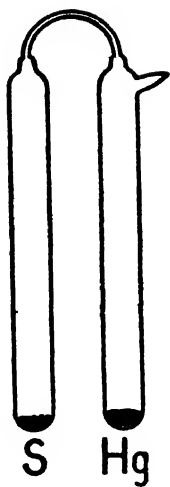


FIG. 15.

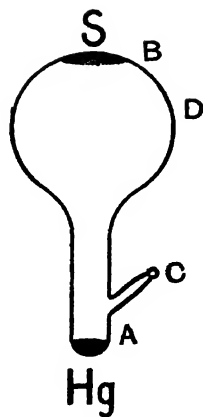


FIG. 17.

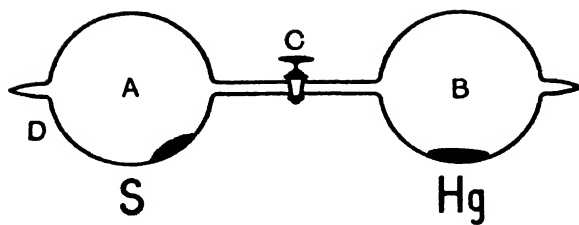


FIG. 16.

would be seen on the sulphur side of the U-tube. But the contrary is the case, as the sulphide is seen to form at first on the surface of the mercury (Hg). The explanation that suggests itself is that the ordinary molecule of sulphur containing 6 to 8 atoms, dissociates and throws off single or double atoms which make their way rapidly through the mercury vapour without wholly combining with it, until they reach the surface of the liquid mercury, when the conditions for chemical interaction are more favourable. If the tube be constricted as at M (Fig. 15), the activity of the sulphur atoms on the mercury surface is stopped, as they encounter the mercury atoms under the most favourable circumstances for combination in the narrow tube at M, and there form the sulphide which is quite visible after long keeping.

It is interesting to note the excessively small quantities of the respective elements that are interacting in this case. The pressure of mercury vapour at  $15^{\circ}$  C. is about  $1\frac{1}{2}$  millionths of an atmosphere, whereas that of sulphur is of the order of one thousandth part of the millionth of an atmosphere.

The same phenomenon was exhibited in an even more striking manner by the following experiment. Two equal bulbs A, B (Fig. 16) were united by a tube containing a finely-ground stop-cock C. A small piece of pure sulphur was put into A, and a small quantity of mercury into B, and the whole exhausted through the side-tube D by either a mercury pump or by the use of charcoal cooled in liquid air. While the exhaustion was going on the sulphur in A was fused, and finally the tube D was sealed off. On shutting the stop-cock C, and allowing the apparatus to stand for some time, the application of a liquid air sponge to any part of the bulb B at once caused the deposition of a mercury mirror, which disappeared on allowing the cooled spot to regain the ordinary temperature. If the same cooling is applied to any part of the bulb A, no deposit takes place; but, if the sulphur has been recently fused so as to get it deposited on a portion of the glass surface in what is called the *utricular* state, then, in a short time a fine film of highly refracting sulphur is seen to have distilled to the cooled part, just like what takes place with the mercury in the other bulb. Now let the stop-cock C be opened for a few seconds and shut again, and the local liquid air cooling on parts of both A and B repeated. On the cooled part of B nothing but mercury will be deposited, as before; but on the cooled part of A a brilliant metallic deposit will be noticed, which is, however, not wholly mercury, for, on heating it with the finger, it is only partially volatilised, the portion which remains being sulphide of mercury. On repeating the operation on another part of A in about a quarter of an hour, all metallic deposition has disappeared. Thus, mercury vapour requires time to react with sulphur, but ultimately all the mercury vapour is removed by the sulphur. The apparatus enables the experiment to be repeated at any time.

Shortly after the discovery of oxygen by Priestley some Dutch physicists began the study of the gases absorbed and given off by living plants; and for this purpose the plants were covered by bell-jars whose lower edge was laid in a channel of mercury. But a difficulty arose, as it was found that the plants in these circumstances soon became sickly and died. Then the remarkable discovery was made that if sulphur was sprinkled over the leaves and the surface of the vessel the deleterious effect of the mercury was overcome and the plants became healthy. Boussingault repeated and confirmed these results in 1868, and made many experiments to elucidate the remedial action of sulphur. He explained this action by pointing out that the poisoning of the plants arose from the presence of mercury vapour, and that as one volume of sulphur vapour was able to combine with six volumes of mercury vapour, the sulphur although less volatile was able effectually to neutralise the deleterious effects of the mercury vapour.

Now, the ratio of the pressure of mercury vapour to that of sulphur at the temperature of  $115^{\circ}\text{C}.$ , when both bodies are in the liquid condition, is as 10 to 1. Seeing the sulphur molecule is  $\text{S}_6$  to  $\text{S}_8$ , one volume of sulphur vapour is sufficient to neutralise or combine with 6 to 8 volumes of mercury vapour, so that an excess of mercury pressure of from 6 to 8 times that of the sulphur vapour can always be removed by combination with the sulphur. If, on the other hand, we compare the relative pressures of mercury at  $100^{\circ}\text{C}.$  to that of solid prismatic sulphur at the same temperature, this ratio is 37 to 1, so that the removal of the mercury vapour at the ordinary temperature, when the pressure ratio is still higher, cannot be fully explained. The effect of air and water vapour complicates the action in the case of plants as the molecules of sulphur and mercury have not the free play they have when no inert gas is present. It would seem that in high vacua the  $\text{S}_2$  molecule of sulphur may be considered as produced by molecular dissociation, and that moving with great rapidity relatively to the mercury gas molecules soon gets at the surface of the liquid mercury and coats it with a thin layer of mercury sulphide, which acts as a trap, stopping the exit of further mercury molecules. The effect of such a coating in preventing the escape of mercury vapour may be shown by the use of an inverted boiling point flask like Fig. 17 containing a layer of fused sulphur at B, and mercury at A. Before and during very complete exhaustion, the mercury at A is kept in liquid air and finally the flask is sealed off at C. On standing at the ordinary temperature, the surface of the mercury gets acted upon by the sulphur, and if the mercury is not shaken so as to crack the film of mercury sulphide, a little sponge of liquid air placed upon the surface at D shows no metallic deposit; but the moment the mercury is slightly shaken to break the surface film of the liquid mercury, metallic deposit is instantly formed by the local cooling. This deposit is not all mercury, but partly sulphide, because on taking away the sponge

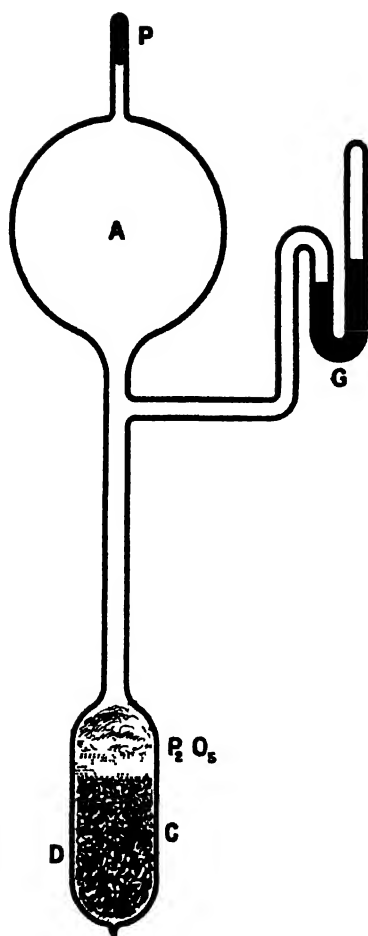


FIG. 18.

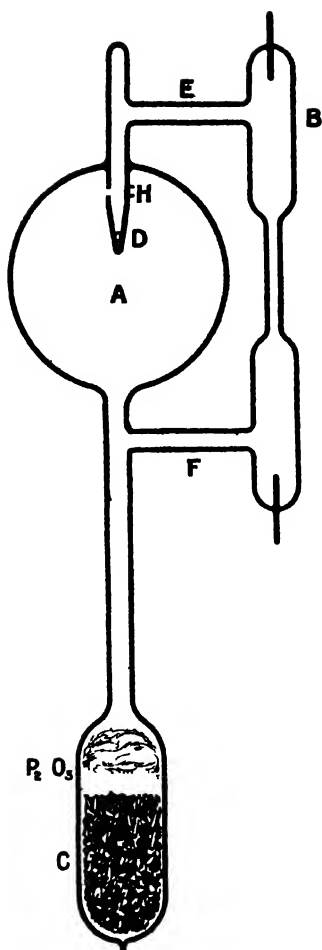


FIG. 19

and heating the cooled spot by contact with the hand, a permanent brown part remains, whereas, if it had been all mercury it would have completely volatilised. On standing for a little time the liquid air cooling causes no metallic mirror, as all the mercury vapour has been removed by combination with the sulphur, and the sulphide film reforms on the mercury, when the experiment may be repeated.

*Phosphoric Action at High Vacua.*

In the Friday Evening address of 1905 an experiment was shown illustrative of the well-known fact that the phosphorous glow caused by oxidation does not take place in dry oxygen at atmospheric pressure, and that it was only when the pressure was very considerably reduced that such action took place. This may be shown more clearly in the following way. A globe (Fig. 18), A, has a small capillary-side tube, P, attached, containing a little phosphorus, that has been melted at its end, and is at the same time connected by another tube to a reservoir, D, containing charcoal covered with a layer of phosphoric anhydride to absorb all traces of moisture. To the side of this tube a small mercury gauge, G, is attached. After the whole vessel is thoroughly exhausted it is filled up to atmospheric pressure with pure oxygen gas and the whole sealed off. On immersing the charcoal bulb in liquid air the pressure falls rapidly to a fraction of a millimetre pressure, and soon the globe A becomes filled with a phosphorescent glow, showing that chemical action is taking place. As the absorption of the oxygen by the charcoal continues the phosphorescence becomes less, and at last disappears, nothing finally filling the bulb but the vapour of phosphorus as it distils from P into the liquid air condenser. Meanwhile the gauge G shows that the pressure at which the phosphorescence begins must be only a fraction of a millimetre, and that it continues at a pressure below what could be measured on the gauge. When the charcoal is taken out of the liquid air, and the temperature allowed to rise, the course of the experiment is inverted, the oxygen occluded in the charcoal being given off, and as it meets the vapour of phosphorus in the bulb A, suddenly combines with it in a few oscillating flashes, and soon all is dark again. The experiment may be repeated after weeks of keeping with the same uniform results. The same thing is also very beautifully shown by the arrangement in Fig. 19. Here the gauge is replaced by a sparking tube B, having free access to the globe A by the tubes E and F, the former having communication by means of the small hole H; D is the phosphorus. The high vacuum at which the glow takes place in the bulb is shown by the character of the discharge taking place in B. A curious phenomenon is observed on stopping the electric discharge; now the glow travels from the bulb along E and F and meets in the middle of B. It looks as if the electric

discharge expelled all the phosphorous vapour from the discharge tube, and that the moving phosphorescent stream is due to the vapour of phosphorus coming back again. While the electric discharge is passing in B, the spectroscope reveals only the oxygen bands.

*Separation of the volatile gases Neon, Hydrogen, Helium.*

Attention has already been called to the selective nature of the absorption when a mixture of gases is presented to cooled charcoal, and it has been noted that the gas obtained from the charcoal after absorption of air has the quantity of oxygen increased from 21 to 50 or 60 per cent. The general law of this absorption is that the lower the boiling point, in other words, the more volatile or less condensable the gas, the less is the absorption. Thus for air, nitrogen with the lower boiling point is not absorbed to so great a degree as oxygen, which has the higher boiling point. This is beautifully shown in the following experiment. A number of spectroscopic tubes connected in series with a large charcoal U-tube, are highly exhausted by cooled charcoal so that the discharge will hardly pass. The charcoal tube is now placed in liquid air, and a slow current of air is allowed to enter the system. The less volatile gases, oxygen, nitrogen, argon, are absorbed by the charcoal, while the more volatile gases, helium, neon, and hydrogen, are allowed to pass. In a short time, when the pressure of the latter gases has risen sufficiently, the first tube begins to glow with the well-known rich orange hue of neon. As the air-absorption progresses, the characteristic discharge of neon and helium gradually extends to the other tubes, the slowness of the current displaying vividly the march of the neon and helium glow. In this connection the sensitivity of the neon tube to induced electric oscillations from a coil of wire placed at right angles to the tube, was shown. This property of neon Professor Fleming makes use of in his ingenious wave-detector for wireless telegraphy—the cymometer.

The most volatile gases being neon, hydrogen and helium, when a charcoal bulb attached to a sparking tube filled with helium, was placed in liquid air, the nature of the luminosity remained unchanged, thus indicating that hardly any absorption had taken place at the temperature of liquid air. But on replacing the liquid air by liquid hydrogen under exhaustion, the pressure was so much reduced that the discharge no longer passed. This observation corroborates the statement already made that the boiling point of hydrogen is a temperature for helium which corresponds with the boiling point of air for hydrogen, and leads us to infer that the boiling point of helium is about  $5^{\circ}$  to  $6^{\circ}$  absolute.

Measurements made in 1902, by what was called the float-method of separation, showed that the atmosphere contained as a minimum one part in 70,000 of neon, and one part in 362,000 of helium.



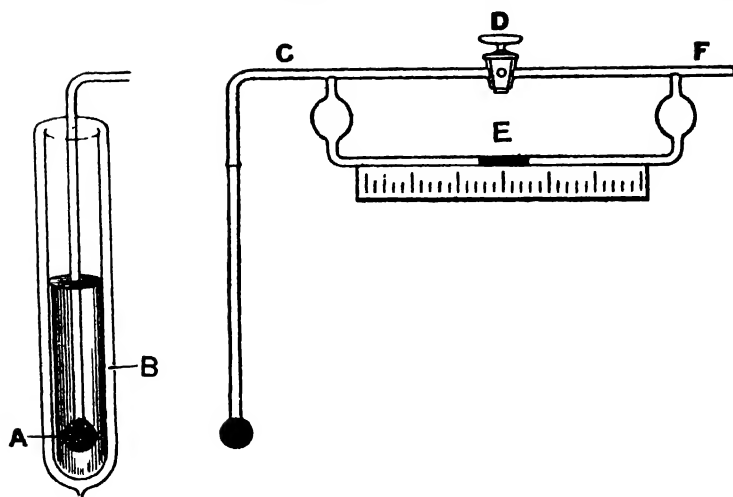


FIG. 20.

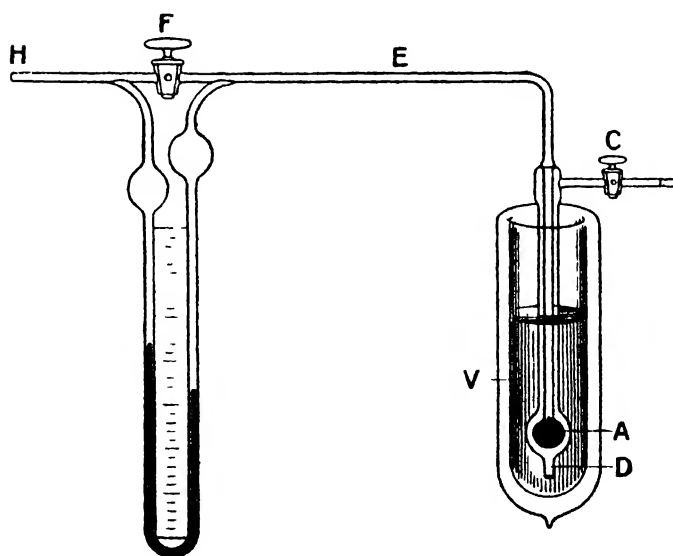


FIG. 21.

Recent determinations by the charcoal method, made by Sir W. Ramsay, give these proportions as one part in 80,790 of neon, and one part in 245,300 of helium or one part in 61,000 of both these gases together. The absorption of 30 litres of air by 500 grammes of charcoal gives a residuary pressure amounting to between 1.4 and 1.5 mm. of mercury pressure; thus representing a partial pressure of unabsorbed gases, helium, neon and hydrogen amounting to  $\frac{1}{5300}$  of the volume of the original air used in the experiment.

*Separation of the less volatile gases, Krypton and Xenon, by Charcoal.*

The method of separating carbonic acid from air shown in the Friday Evening Address for 1905 is equally applicable to the separation of krypton and xenon. A current of air passes through a series of tubes immersed in liquid air for the purpose of purification, the final tube containing cotton wool in order to retain any dust of the solid condensed impurities. This pure air is passed through a tube containing about 100 grammes of charcoal, the current being maintained for at least 24 hours. The charcoal tube is now removed and placed in solid carbonic acid, any gas coming off being allowed to escape. The gas remaining in the charcoal at  $-78^{\circ}\text{C}$ . is now got out by heating and exhaustion, and all the carbon compounds and oxygen removed from it. The remaining gas, nitrogen containing krypton and xenon, is separated into its constituents by condensation and fractionation. Instead of passing a current of air over charcoal at  $-183^{\circ}\text{C}$ ., a few hundred grammes of charcoal may be covered with old liquid air, and the latter allowed to evaporate in a silver vacuum vessel, the gases remaining in the charcoal being separated as above. In this way krypton and xenon are readily separated from air and spectrum tubes easily prepared.

*Charcoal Thermometer and Calorimeter.*

Charcoal saturated with gases at low temperatures may be used as a thermoscope or calorimeter. Attention has been called to the law of absorption, that when the volume is constant, the pressure falls very rapidly with the temperature; in fact, the curve connecting them, when pressure is plotted as ordinate to temperature as abscissa, drops almost vertically as the temperature diminishes to the absolute zero, and a similar relation holds for the volume absorption at constant pressure. Hence, a small change of temperature is accompanied by a great change of pressure or volume absorption as the case may be. This was exemplified in the following experiment. A charcoal bulb A (Fig. 20) previously saturated with air at  $-185^{\circ}\text{C}$ . or hydrogen at  $-253^{\circ}\text{C}$ . at any required pressure, the most convenient being

atmospheric pressure, was immersed in a bath B of the corresponding liquefied gas contained in a vacuum-jacketed vessel; and a tube C was led from it to a Leslie thermometer containing a sulphuric acid cylinder used as a registration instrument for volume. The gauge consisted of a U-tube, with bulbs on each side, to prevent any sudden sucking back of the drop of sulphuric acid E, renders visible the slightest alteration of the volume of gas occluded in the charcoal. The upper ends of the U-tube were connected by a by-pass containing a stop-cock D. On shutting this stop-cock after the complete saturation of the charcoal with air has been effected, equilibrium of pressure between C and F could be obtained, while the sulphuric acid drop E occupied a convenient position in the gauge. On the approach of a candle-flame to the charcoal bulb, the gauge immediately showed a considerable expansion, notwithstanding that the radiant heat had to traverse a considerable quantity of liquefied gas, and several thicknesses of glass tubing. In the same manner a beam of light thrown on the charcoal bulb when charged with hydrogen instead of air immediately affected the gauge in a striking way.

The apparatus can be rendered still more sensitive by the following device (Fig. 21). The charcoal bulb A, saturated with air at  $-185^{\circ}\text{C}$ ., is surrounded with another larger bulb giving an annular space that can be filled with liquid air by opening the stop-cock C, the orifice D being open while immersed in a large vacuum-jacketed reservoir, V, of liquid air. The tube E leading from A passes to a sulphuric acid manometer, with by-pass and stop-cock, F, as before, thence to the open end H. The apparatus works thus: Before the radiant beam is turned on A, the annular space between the bulbs is cleared of liquid by blowing a little air through the tube C, and shutting the stop-cock, thus forcing the liquid air out by the aperture D. The charcoal bulb is now surrounded by an atmosphere of liquid air vapour, or hydrogen, as the case may be, maintained at the boiling point by the liquid in V. In these circumstances the maximum effect of any heat given to the charcoal bulb is obtained. The effects are magnified two or three times compared with those given by the charcoal bulb left in direct contact with the liquid.

The special value of this instrument for thermometric measurements is that it becomes more sensitive as the temperature falls, thus placing in our hands a most efficient thermometer for the lowest temperatures which can possibly be reached. Thus, when the charcoal is saturated with hydrogen gas at the boiling point of hydrogen, the instrument has its maximum delicacy under ordinary circumstances; but provided helium was absorbed in charcoal at and below the temperature of solid hydrogen, then we can predict that the instrument would be still more sensitive to radiant energy.

If, further, the charcoal occupies an annular space surrounding another smaller bulb, into the interior of which any small heated

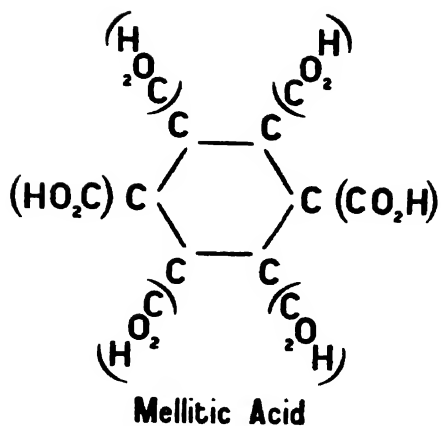


FIG. 22.—Graphical Formula of Mellitic Acid.

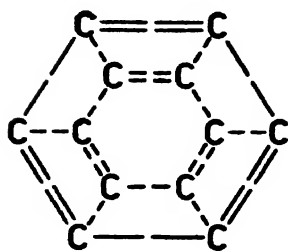


FIG. 23.—Graphical Formula of Charcoal Molecule.

object is inserted, the apparatus becomes a very sensitive calorimeter.

Much investigation is still necessary to clear up the nature of the various charcoals and their properties. One chemical character they possess, and that is that, by powerful oxidising agents like concentrated nitric acid or permanganate of potash, they seem all capable of giving a greater or less yield of an acid called Mellitic Acid, the graphical formula of which is represented in (Fig. 22), which occurs in nature as the aluminium salt, commonly called Honey-stone. This acid, we know, is a derivative of benzol, and its production from charcoal suggests that the latter has a structure of double benzene rings, each containing twelve atoms of carbon such as is shown in (Fig. 23). This gives a fundamental molecule containing a large number of latent valences available for chemical or physical combination, and this structure may have something to do with the general absorptive power of charcoal.

[The Professor thanked his assistants, Mr. R. N. Lennox and Mr. J. W. Heath, for valuable aid in the conduct of these experiments.]

Friday, March 22, 1907.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. P.C. D.C.L.  
F.R.S., President, in the Chair.

PROFESSOR J. J. THOMSON, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,  
Professor of Natural Philosophy *R.I.*

*Rays of Positive Electricity.*

IN 1886 Goldstein discovered that when the cathode in a discharge-tube is perforated, rays pass through the openings and produce luminosity in the gas behind the cathode; the colour of the light depends on the gas with which the tube is filled, and coincides with the colour of the velvety glow which occurs immediately in front of the cathode. The appearance of these rays is indicated in Fig. 1, the anode being to the left of the cathode K.K. Since the rays appeared through narrow channels in the cathode, Goldstein called them "Kanalstrahlen"; now that we know more about their nature, "positive rays" would, I think, be a more appropriate name. Goldstein showed that a magnetic force which would deflect cathode rays to a very considerable extent was quite without effect on the "Kanalstrahlen." By using intense magnetic fields, W. Wien showed that these rays could be deflected, and that the deflection was in the opposite direction to that of the cathode rays, indicating that these rays carry a positive charge of electricity. This was confirmed by measuring the electrical charge received by a vessel into which the rays passed through a small hole, and also by observing the direction in which they are deflected by an electric force. By measuring the deflections under magnetic and electric forces, Wien found by the usual



FIG. 1.

methods the value of  $\frac{e}{m}$  and the velocity of the rays. He found for the maximum value of  $\frac{e}{m}$  the value of  $10^4$ , which is the same as that for an atom of hydrogen in the electrolysis of solutions. A valuable

summary of the properties of these rays is contained in a paper by Ewers.\*

As these rays seem the most promising subjects for investigating the nature of positive electricity, I have made a series of determinations of the values of  $\frac{e}{m}$  for positive rays under different conditions. The results of these I will now proceed to describe.

### *Apparatus.*

*Screen used to Detect the Rays.*—The rays were detected and their position determined by the phosphorescence they produced on a screen at the end of the discharge-tube. A considerable number of substances were examined to find the one which would fluoresce most brightly under the action of the rays. As the result of these trials willemite was selected. This was ground to a very fine powder and dusted uniformly over a flat plate of glass. Considerable trouble was found in obtaining a suitable substance to make the powder adhere to the glass. All gums, etc., when bombarded by the rays are liable to give off gas; this renders them useless for work in vacuum-tubes. The method finally adopted was to smear a thin layer of "water-glass" (sodium-silicate) over the glass plate, and then dust the powdered willemite over this layer and allow the water-glass to dry slowly before fastening the plate to the end of the tube.

The form of tube adopted is shown in Fig. 2. A hole is bored through the cathode, and this hole leads to a very fine tube F. The bore of this tube is made as fine as possible, so as to get a small well-defined fluorescent patch on the screen. These tubes were either carefully-made glass tubes, or else the hollow thin needles used for hypodermic injections, which I find answer excellently for this purpose. After getting through the needle, the positive rays on their way down the tube pass between two parallel aluminium plates A A. These plates are vertical, so that when they are maintained at different potentials the rays are subject to a horizontal electric force, which produces a horizontal deflection of the patch of light on the screen. The part of the tube containing the parallel aluminium plates is narrowed as much as possible, and passes between the poles P P of a powerful electromagnet of the Du Bois type. The poles of this magnet are as close together as the glass tube will permit, and are arranged so that the lines of magnetic force are horizontal and at right angles to the path of the rays. The magnetic force produces a vertical deflection of the patch of phosphorescence on the screen. To bend the positive rays it is necessary to use strong magnetic fields, and if any of the lines of force were to stray into the discharge-tube

in front of the cathode they would distort the discharge in that part of the tube. This distortion might affect the position of the phosphorescent patch on the screen, so that unless we shield the discharge-tube we cannot be sure that the displacement of the phosphorescence is entirely due to the electric and magnetic fields acting on the positive rays after they have emerged from behind the cathode.

To screen off the magnetic field the tube was placed in a soft iron vessel *W* with a hole knocked in the bottom, through which the part of the tube behind the cathode was pushed. Behind the vessel a thick plate of soft iron with a hole bored through it was placed, and behind this again as many thin plates of soft iron, such as are used

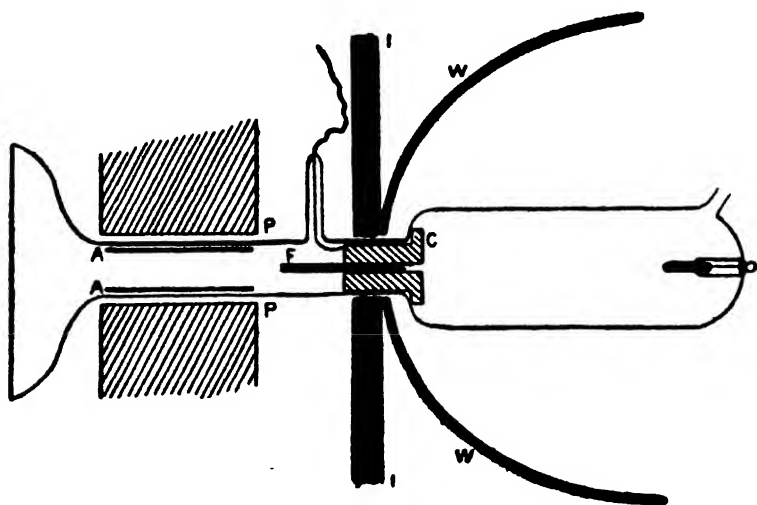


FIG. 2.

for transformers, as there was room for, were packed. When this was done it was found that the magnet produced no perceptible effect on the discharge in front of the cathode.

The object of the experiments was to determine the value of  $\frac{e}{m}$  by observing the deflection produced by magnetic and electric fields. When the rays were undeflected they produced a bright spot on the screen; when the rays passed through electric and magnetic fields, the spot was not simply deflected to another place, but was drawn out into bands or patches, sometimes covering a considerable area. To determine the velocity of the rays, and the value of  $\frac{e}{m}$ , it was necessary to have a record of the shape of these patches. This might



have been done by substituting a photographic plate for the willemite screen. This, however, was not the method adopted, as, in addition to other inconveniences, it involves opening the tube and re-pumping for each observation, a procedure which would have involved a great expenditure of time. The method actually adopted was as follows: The tube was placed in a dark room from which all light was carefully excluded, the tube itself being painted over, so that no light escaped from it. Under these circumstances the phosphorescence on the screen appeared bright and its boundaries well defined. The observer traced in Indian ink on the outside of the thin flat screen the outline of the phosphorescence. When this had been satisfactorily accomplished the discharge was stopped, the light admitted into the room, and the pattern on the screen transferred to tracing-paper; the deviations were then measured on these tracings.

*Calculation of the Magnetic and Electric Deviation of the Rays.*

If we assume the electric field to be uniform between the plates and zero outside them, then we can easily show that  $x$ , the horizontal deflection of a ray whose charge is  $e$ , mass  $m$ , and velocity  $v$ , is given by the equation

$$x = \frac{1}{2} X \frac{e}{m v^2} l (l + 2d),$$

where  $X$  is the force between the plates,  $l$  the length of path of the rays between the plates, and  $d$  the distance of the screen from the nearer end of the parallel plates.

To find the deflection due to the magnetic field, we have, if  $\rho$  is the radius of curvature of the path at a point where the magnetic force is  $H$ .

$$\frac{m v^2}{\rho} = H e v,$$

or

$$\frac{1}{\rho} = \frac{e}{m v} H.$$

If  $y$  is the vertical displacement of the particle, we have

$$\frac{1}{\rho} = \frac{d^2 y}{dz^2} \text{ approximately,}$$

where  $z$  is measured along the path of the ray. Hence

$$\frac{d^2 y}{dz^2} = \frac{e}{m v} H ;$$

$$y = \frac{e}{m v} \left[ \int_0^{z+d} \int_0^z H dz \right] \dots \dots (1)$$

In these strong fields there are considerable variations of  $H$  along the path, so that to calculate the integrals we should have to map out the value of  $H$  along the path of the ray. This would be a very laborious process, and it was rendered unnecessary by the following simple method, which, while not involving anything like the labour of the direct method, gives much more accurate results. The method is shown in Fig. 3. The part of the tube through which the rays pass was cut off, and a metal rod placed so that its tip  $Z$  coincided with the aperture of the narrow tube through which the positive rays had emerged. A very fine wire soldered to the end of this tube passed over a light pulley, and carried a weight at the free end. The pulley was supported by a screw, by means of which it could be raised or lowered; a known current passed through the wire, entering it at  $Z$

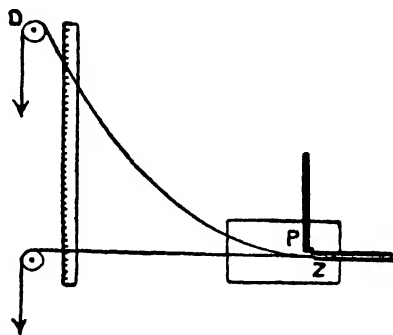


FIG. 3.

and leaving it through the pulley. The pulley was first placed so that the path of the stretched wire when undeflected by a magnetic field coincided with the path of the undeflected rays. A vertical scale, whose edge was at the same distance from the opening through which the rays emerge as the screen on which the phosphorescence had been observed, was placed just behind the wire, and was read by a reading microscope with a micrometer eyepiece. When the magnetic field was put on, the wire was deflected; and if  $T$  is the tension of the wire,  $\rho$  the radius or curvature into which it is bent,  $i$  the current through the wire,

$$\frac{T}{\rho} = H i;$$

or, if  $y_1$  is the vertical displacement of the wire,

$$\frac{d^2 y_1}{dz^2} = \frac{i}{T} H.$$

Now if  $\frac{dy_1}{dz} = 0$  when  $z = 0$  we have, if  $y_1$  is the displacement of the wire at the scale,

$$y_1 = \frac{i}{T} \int_0^1 \cdot \int_0^z H dz \quad . . . . . (2)$$

Hence, comparing (1) and (2) we have

$$\frac{y}{y_1} = \frac{\frac{e}{mv}}{\frac{i}{T}}, \quad . . . . . (3)$$

a relation from which the magnetic force is eliminated. To ensure that the tangent to the wire is horizontal when  $z = 0$ , the following method is used. P is a chisel-edge carried by a screw and placed about 1 mm. in front of the fixed end of the wire; this is adjusted so that when the magnetic field is not on, the wire just touches the edge; this can be ascertained by making the contact with the wire complete an electric circuit in which a bell is placed. When the magnetic field is put on the wire is pulled off from the edge, and the tangent at  $z = 0$  is no longer horizontal; it can, however, be brought horizontal by raising or lowering the pulley D until the wire is again in contact with P, which can be ascertained again by the ringing of the bell. Then  $y_1$  is the vertical distance between the point where the wire now crosses the edge of the scale and the point where it crossed it before the magnetic field was put on. Since  $y$ ,  $y_1$ ,  $i$ , and  $T$  can easily be measured, equation (3) gives us the value of  $\frac{e}{mv}$ , while the deflection under the electric force gives the value of  $\frac{e}{mv_2}$ .

If  $y$  is the vertical displacement of the patch of phosphorescent light on the screen produced by the magnetic field,  $x$  the horizontal displacement due to the electrostatic field, we see that

$$y = \frac{y_1}{\left(\frac{i}{T}\right)} \frac{e}{mv} = B \frac{e}{mv},$$

$$x = A \frac{e}{mv^2},$$

where A and B are constants depending on the position of the screen and the magnitudes of the electric and magnetic forces. These quantities can be calculated by means of the equations just given.

Since

$$\frac{y}{x} = \frac{B}{A} v,$$

$$\frac{y^2}{x} = \frac{B^2}{A} \frac{m}{e}.$$

We see that if the pencil is made up of rays having a constant velocity, but having all values of  $\frac{e}{m}$  up to a maximum value, the spot of light will be spread out by the magnetic and electric fields into a straight line extending a finite distance from the origin. While if it is made up of two sets of rays, one having the velocity  $v_1$ , the other the velocity  $v_2$ , the spot will be drawn out into two straight lines as in Fig. 4.

If  $\frac{e}{m}$  is constant and the velocities have all values up to a maximum, the spot of light will be spread out into a portion of a parabola, as indicated in Fig. 5.



FIG. 4.



FIG. 5.

We shall later on give examples of each of these cases.

The discharge was produced by means of a large induction coil, giving a spark of about 50 cm. in air, with a vibrating make and break apparatus. Many tubes were used in the course of the investigation; the dimensions of these varied slightly. The distance of the screen from the hole from which the rays emerged was about 9 cm., the length of the parallel plates about 3 cm., and the distance between them .3 cm.

*Properties of the Positive Rays when the Pressure is not exceedingly low.*

The appearance of the phosphorescent patch after deflection in the electric and magnetic fields depends greatly upon the pressure of the gas. I will begin by considering the case when the pressure is comparatively high, say of the order of  $\frac{1}{10}$  mm. At these pressures, though the walls of the tube in front of the cathode were covered with bright phosphorescence and the dark space extended right

up to the walls of the tube, and was several centimetres thick, traces of the positive column could be detected in the neighbourhood of the anode. I will first take the case where the tube was filled with air. Special precautions were taken to free the air from hydrogen; it

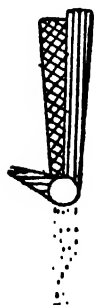


FIG. 6.

was carefully dried, and a subsidiary discharge-tube, having a cathode made of the liquid alloy of sodium and potassium, was fused on to the main tube. When the discharge passes from such a cathode it absorbs hydrogen. The discharge was sent through this tube at the lowest pressure at which enough light was produced in the gas to give a visible spectrum, until the hydrogen lines disappeared and the only lines visible were those of nitrogen and mercury vapour. This pressure was a little higher than that used for the investigation of the positive rays, but a pump or two was sufficient to bring the pressure down to this value. The appearance of the phosphorescence on the screen when the rays were deflected by magnetic and electric forces separately and conjointly

is shown in Fig. 6.

The deflection under magnetic force alone is indicated by vertical shading, under electric force alone by horizontal shading, and under the two combined by cross shading.

The spot of phosphorescence is drawn out into a band on either side of its original position. The upper portion, which is very much the brighter, is deflected in the direction which indicates that the phosphorescence is produced by rays having a positive charge; the lower portion (indicated by dots in the figure), which though faint is quite perceptible on the willemite screen, is deflected as if *the rays carried a negative charge*. The length of the lower portion is somewhat shorter than that of the upper one, but is quite comparable with it. The intensity of the luminosity in the upper portion is at these pressures quite continuous; no abrupt variations such as would show themselves as bright patches could be detected, although, as will be seen later on, these make their appearance at lower pressures. Considering for the present the upper portion, the straightness of the edges shows that the velocity of the rays is approximately constant, while the values of  $\frac{e}{m}$  range from zero at the undeflected portion to the value approximately equal to  $10^4$  at the top of the deflected band. This value of  $\frac{e}{m}$  is equal to that for a charged hydrogen atom, and, moreover, there was no specially great luminosity in the positions corresponding to  $\frac{e}{m} = \frac{10^4}{14}$  and  $\frac{10^4}{16}$ , the values for rays carried by nitrogen or oxygen atoms, though these places were carefully scrutinised. As hydrogen when present as an impurity in the tube has a tendency

to accumulate near the cathode, the following experiment was tried to see whether the Kanalstrahlen were produced from traces of hydrogen in the tube. The discharge was sent through the tube in the opposite direction, i.e. so that the perforated electrode was the anode, the electric and magnetic fields being kept on. When the discharge passed in this way there was, of course, no luminosity on the screen; on reversing the coil again, so that the perforated electrode was the cathode, the luminosity flashed out instantly, presenting exactly the same appearance as it had done when the tube had been running for some time with the perforated electrode as cathode.

The fact that a spot of light produced by the undeflected positive rays is under the action of electric and magnetic forces drawn out into a continuous band was observed by W. Wien, who was the first to measure the deflection of the positive rays under electric and magnetic forces. The values of  $\frac{e}{m}$  obtained from the deflections of

various parts of this band range continuously from zero, the value corresponding to the undeflected portion, to  $10^4$ , the value corresponding to those most deflected. Wien explained this by the hypothesis that the charged particles which make up the positive rays act as nuclei, round which molecules of the gas through which the rays pass condense, so that very complex systems made up of a very large number of molecules get mixed up with the particles forming the positive rays, and that it is these heavy and cumbrous systems which give rise to that part of the luminosity which is only slightly deflected. I think that the constancy of the velocity of the rays, indicated by the straight edges of the deflected band, is a strong argument against this explanation, and that the existence of the negative rays is conclusive against it. These negatively electrified rays, which form the faintly luminous portion of the phosphorescence indicated in Fig. 6, are not cathode rays. The magnitude of their deflection shows that

the ratio of  $\frac{e}{m}$  for these rays, instead of being as great as  $1.7 \times 10^7$ ,

the value for cathode rays, is less than  $10^4$ . The particles forming these rays are thus comparable in size with those which form the positive rays. The existence of these negatively electrified rays suggests at once an explanation, which I think is the true one, of the continuous band into which the spot of phosphorescence is drawn out by the electric and magnetic fields. The values of  $\frac{e}{m}$  which are de-

termined by this method are really the mean values of  $\frac{e}{m}$ , while the particle is in the electric and magnetic fields. If the particles are for a part of their course through these fields without charge, they will not during this part of their course be deflected, and in consequence the deflections observed on the screen, and conse-

quently the values of  $\frac{e}{m}$ , will be smaller than if the particle had retained its charge during the whole of its career. Thus, suppose that some of the particles constituting the positive rays, after starting with a positive charge, get this charge neutralised by attracting to them a negatively electrified corpuscle, the mass of the corpuscle is so small in comparison with that of the particle constituting the positive ray that the addition of the particle will not appreciably diminish the velocity of the positive particle. Some of these neutralised particles may get positively ionised again by collision, while others may get a negative charge by the adhesion to them of another corpuscle, and this process might be repeated during the course of the particle. Thus there would be among the rays some which were for part of their course unelectrified, at other parts positively electrified, and at other parts negatively electrified. Thus the mean value of  $\frac{e}{m}$  might have all values ranging from  $a$ , its initial value, to  $-a'$ , where  $a'$  might be only a little less than  $a$ . This is just what we observe, and when we remember that the gas through which the rays are passing is ionised, and contains a large number of corpuscles, it is, I think, what we should expect.

At very low pressures, when there are very few ions in the gas, this continuous band stretching from the origin is replaced by discontinuous patches.

#### *Positive Rays in Hydrogen.*

In hydrogen, when the pressure is not too low, the brightness of the phosphorescent patch is greater than in air at the same pressure; the shape of the deflected phosphorescence is markedly different from that in air. In air, the deflected phosphorescence is usually a straight



FIG. 7.



FIG. 8.

band, whereas in hydrogen the boundary of the most deflected side is distinctly curved and is concave to the undeflected position. The appearance of the deflected phosphorescence is indicated in Fig. 7.

The result indicated in Fig. 8, which was also obtained with hydrogen, shows that we have here a mixture of two bands, as indi-

cated in Fig. 4, the two bands being produced by carriers having different maximum values of  $\frac{e}{m}$ . The greatest value of  $\frac{e}{m}$  obtained with hydrogen was the same as in air,  $1.2 \times 10^4$ , the velocity was  $1.8 \times 10^8$  cm. per sec. The presence of the second band indicates that mixed with these we have another set of carriers, for which the maximum value  $\frac{e}{m}$  is half that in the other band, i.e.  $5 \times 10^3$ . The curvature of the boundary generally observed is due to the admixture of these two rays.

### *Positive Rays in Helium.*

In helium the phosphorescence is bright, and the deflected patch has in general the curved outline observed in hydrogen. I was fortunate enough, however, to find a stage in which the deflected patch was split up into two distinct bands, as shown in Fig. 9. The maximum value of  $\frac{e}{m}$  in the band *a* was  $1.2 \times 10^4$ , the same as in air and hydrogen, and the velocity was  $1.8 \times 10^8$ ; while the maximum value of  $\frac{e}{m}$  in band *b* was almost exactly one quarter of that in *a* (i.e.  $2.9 \times 10^3$ ). As the atomic weight of helium is four times that of hydrogen, this result indicates that the carriers which produce the band *b* are atoms of helium. This result is interesting because it is the only case



FIG. 9.

(apart from hydrogen) in which I have found values of  $\frac{e}{m}$  corresponding to the atomic weight of the gas; and even in the case of helium, when the pressure in the discharge-tube is very low and the electric field very intense, the characteristic rays with  $\frac{e}{m} = 2.9 \times 10^3$  sometimes disappear, and, as in all the gases I have tried, we get two sets of rays, for one set of which  $\frac{e}{m} = 10^4$  and for the other  $5 \times 10^3$ .

Although the helium had been carefully purified from hydrogen, the band *a* (for which  $\frac{e}{m} = 10^4$ ) was generally the brighter of the two. The case of helium is an interesting one; for the class of positive rays, known as the *a* rays, which are given off by radioactive substances, would *a priori* seem to consist most probably of helium, since helium is one of the products of disintegration of these substances. The value of  $\frac{e}{m}$  for these substances is  $5 \times 10^3$ , where we have seen that in helium it is possible to obtain rays for which  $\frac{e}{m} = 2.9 \times$



$10^3$ . It is true that, at very low pressures and with strong electric fields, we get rays for which  $\frac{e}{m} = 5 \times 10^3$ ; but this is not a peculiarity of helium; all the gases which I have tried show exactly the same effect.

### *Argon.*

When the discharge passed through argon, the effects observed were very similar to those occurring in air. The sides were perhaps a little more curved, and there was a tendency for bright spots to develop. The measurements of the electric and magnetic deflection of these spots gave  $\frac{e}{m} = 10^4$ , the value obtained for other cases. There was no appreciable increase of luminosity in the positions corresponding to  $\frac{e}{m} = 10^4$ , as there would have been if an appreciable number of the carriers had been argon atoms.

### *Positive Rays in Gases at very low pressures.*

As the pressure of the gas in the discharge-tube is gradually reduced, the appearance of the deflected phosphorescence changes: instead of forming a continuous band, the phosphorescence breaks up into two isolated patches; that part of the phosphorescence in which the deflection was very small disappears, as also does the phosphorescence produced by the negatively electrified portion of the rays.

In the earlier experiments considerable difficulty was experienced in working at these very low pressures: for when the pressure was reduced sufficiently to get the effects just described, the discharge passed through the tube with such difficulty, that in a very few seconds after this stage was reached sparks passed from the inside to the outside of the tube, perforating the glass and destroying the vacuum. In spite of all precautions, such as earthing the cathode and all conductors in its neighbourhood, perforation took place too quickly to permit measurements of the deflection of the phosphorescence.

This difficulty was overcome by taking advantage of the fact that, when the cathode is made of a very electropositive metal, the discharge passes with much greater ease than when the cathode is made of aluminium or platinum. The electropositive metals used for the cathode were: (1) the liquid alloy of sodium and potassium which was smeared over the cathode, and (2) calcium, a thin plate of which was affixed to the front of the cathode. With these cathodes, the pressure in the tube could be reduced to very low values without making the discharge so difficult as to lead to perforation of the tube by sparking, and accurate measurements of the position of the patches of phosphorescence could be obtained at leisure.

The results obtained at these low pressures are very interesting. Whatever kind of gas may be used to fill the tube, or whatever the nature of the electrode, the deflected phosphorescence splits up into two patches. For one of these patches the maximum value of  $\frac{e}{m}$  is about  $10^4$ , the value for the hydrogen atom; while the value for the other patch is about  $5 \times 10^3$ , the value for  $\alpha$  particles or the hydrogen

Hydrogen

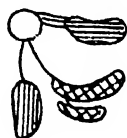


FIG. 10.

Helium



FIG. 11.

Air



FIG. 12.

molecule. Examples of the appearance of this phosphorescence are given in Figs. 10, 11 and 12. In Fig. 12 the magnetic force was reversed.

The differences in the appearance are due to differences in the pressure rather than to differences in the gas; for at slightly higher pressures than that corresponding to Fig. 12, the appearance shown in Figs. 10 and 11 can be obtained in air. In all these cases the more deflected patch corresponds to a value of about  $10^4$  for  $\frac{e}{m}$  while  $\frac{e}{m}$  for the less deflected patch is about  $5 \times 10^3$ .

It will be noticed that in Fig. 11 there is no trace in the helium tube of rays for which  $\frac{e}{m} = 2.5 \times 10^3$ , which were found in helium tubes at higher pressures; at intermediate pressures there are *three* distinct patches of helium, for the first of which  $\frac{e}{m} = 10^4$ , for the second  $\frac{e}{m} = 5 \times 10^3$ , and for the third  $\frac{e}{m} = 2.5 \times 10^3$  approximately.

Helium is a case where there are characteristic rays—i.e. rays for which  $\frac{e}{m} = \frac{10^4}{M}$ , where  $M$  is the atomic weight of the gas, when the discharge potential is comparatively small, and not when, as at very low pressures, the discharge potential is very large. I think it very probable that, if we could produce the positive rays with much smaller potential differences than those used in these experiments, we might get the characteristic rays for other gases. I am at present investigating with this object the positive rays produced when the perforated cathode is, as in Wehnelt's method, coated with lime, when a potential

difference of 100 volts or less is able to produce positive rays. The interest of the experiments at very low pressures lies in the fact that in this case the rays are the same whatever gas may be used to fill the tube; the characteristic rays of the gas disappear, and we get the same kind of carriers for all substances.

I would especially call attention to the simplicity of the effects produced at these low pressures; only two patches of phosphorescence are visible. This is, I think, an important matter in connection with the interpretation of these results; for at these low pressures we have to deal, not only with the gas with which the tube was originally filled, but also with the gas which is given off by the electrodes and the walls of the tube during the discharge; and it might be urged that at these low pressures the tube contained nothing but hydrogen given out by the electrodes. I do not think this explanation is feasible, for the following reasons:—

(1) The gas developed during the discharge is not wholly hydrogen; if the discharge is kept passing long enough to develop so much gas that the discharge through the gas is sufficiently luminous to be observed by a spectroscope, the spectrum always showed, in addition to the hydrogen lines, the nitrogen bands; indeed, the latter were generally the most conspicuous part of the spectrum. If the phosphorescent screen on which the positive rays impinge is observed during the time this is being given off, the changes which take place in the appearance of the screen are as follows: If, to begin with, the pressure is so low that the phosphorescent patches are reduced to two bright spots, then, as the pressure begins to go up owing to the evolution of the gas, the deflection of the spots increases. This is owing to the reduction in the velocity of the rays consequent upon the reduction of the potential difference between the terminals of the tube, as at this stage an increase in the pressure facilitates the passage of the discharge. In addition to the increase in the displacement there is an increase in the area of the spots giving a greater range of values of  $\frac{e}{m}$ ; this is owing to the increase in the number of collisions made by the particles in the rays on their way to the screen. As more and more gas is evolved the patches get larger, and finally overlap; the existence of the second patch being indicated by a diminution in the brightness of the phosphorescence at places outside its boundary. As the pressure increases the luminosity gets more and more continuous, and we finally get to the continuous band, as shown in Fig. 6. At this stage it is probable that there may be enough luminosity to give a spectrum showing the nitrogen lines, indicating that a considerable part of the gas in the tube is air. It is especially to be noted that during this process, when gas was coming into the tube, there has been no development of patches in the phosphorescence indicating the presence of new rays; on the contrary, one type of

carrier—that corresponding to  $\frac{e}{m} = 5 \times 10^3$ —has disappeared. The presence of the nitrogen bands in the spectrum shows that nitrogen is carrying part of the discharge, and yet there are no rays characteristic of nitrogen to be observed on the screen; a proof, it seems to me, that different gases may be made by strong electric fields to give off the same kind of carriers of positive electricity.

Another result, which shows that the positive rays are the same although the gases are different, is the following. The tube was pumped until the pressure was much too low for the discharge to pass, then small quantities of the following gases were put into the tube: air, carbonic oxide, hydrogen, helium, neon (for which I am indebted to the kindness of Sir James Dewar); the quantity admitted was adjusted so that it was sufficient to cause the discharge to pass, and yet did not raise the pressure beyond the point where the phosphorescence is discontinuous. In every case there were patches corresponding to  $\frac{e}{m} = 10^4$ ,  $\frac{e}{m} = 5 \times 10^3$ , and except with helium these were the only patches; in helium, in addition to the two already mentioned, there was a third patch for which  $\frac{e}{m} = 2.5 \times 10^3$ .

I also tried another method of ensuring that at these low pressures there were other gases besides hydrogen in the tube. I filled the tube with helium, and after exhausting to a fairly low pressure by means of the mercury pump, I performed the last stages of the exhaustion by means of charcoal cooled with liquid air. This charcoal absorbs very little helium in comparison with other gases; so that it is certain that there was helium in the tube. The appearance of the phosphorescent screen of tubes exhausted in this way did not differ from those exhausted solely by the pump.

The most obvious explanation of these effects seems to me to be, that under very intense electric fields different substances give out particles charged with positive electricity, and that these particles are independent of the nature of the gas from which they originate. These particles are, as far as we know at present, of two kinds; for one kind  $\frac{e}{m}$  has the value of  $10^4$ , that of an atom of hydrogen; for the other kind  $\frac{e}{m}$  has half this value, i.e. it has the same value as for the  $\alpha$  particles from radioactive substances.

This agreement in the maximum value of  $\frac{e}{m}$  at different pressures is a proof that this is a true maximum, and that there are not other more deflected rays not strong enough to produce visible phosphorescence; for if this were the case—i.e. if the value of  $\frac{e}{m}$  for a particle

that had never lost its charge temporarily by collision were greater than  $10^4$ —we should expect to get larger values for  $\frac{\theta}{m}$  at low pressures than at high.

I have much pleasure in thanking my assistant, Mr. E. Everett, for the assistance he has given me in these experiments.

[J. J. T.]

Friday, June 7, 1907.

THE RIGHT HON. LORD KELVIN, O.M. G.C.V.O. P.C. D.C.L.  
LL.D. D.Sc. F.R.S., in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,  
Fullerian Professor of Chemistry, R.I.

*Studies in High Vacua and Helium at Low Temperatures.*

IN a former lecture the production of very high vacua by means of charcoal absorption at the temperatures of liquid air and liquid hydrogen was discussed. With this new means of research, we shall now follow its application in various directions. We live in an age characterised by volume and rapidity of publication, in which scientific literature takes its place, so that science is now burdened with much that in former days would have been confided to the waste-paper basket. There is a type of the modern scientist who needs to be continually before the public, and the result is the appearance of immature communications often loaded with needlessly endless details. The foundations of scientific research in our time would seem to be not a little undermined; the tendency being to regard quantity and not quality of output. In these pioneer studies we shall be content to describe the general lines of this investigation, omitting for the present any reference to refinement of details.

High vacua and helium might not appear to have much to do with each other, but, as we shall see, they are intimately connected. Immediately after the liquefaction of hydrogen by regenerative expansion in 1896, I attacked the problem of the liquefaction of helium, following by strict thermo-dynamic analogy the process that had succeeded with hydrogen.\* The hydrogen process was as follows: hydrogen at a pressure of 180 atmospheres cooled down to  $-205^{\circ}\text{C.}$ , was made to issue, at the rate of about 15 cubic feet per minute, from a nozzle terminating a long spiral coil of copper pipe placed in a silvered glass vacuum vessel having a spiral tube connected with the interior. After five minutes' circulation liquid hydrogen began to drop from the end of the spiral tube, and when the liquid was evaporated under exhaustion, it froze into a white frothy mass of solid hydrogen, presenting an appearance quite different from the common belief that in this condition it would in all probability

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\* For full description see Presidential Address, British Association, 1902.

possess metallic lustre. The density of liquid hydrogen at its boiling point ( $-252^{\circ}\cdot 5$  C. or  $20^{\circ}\cdot 5$  Ab.), was found to be about  $0\cdot 07$ , so that liquid hydrogen was about six times lighter than the lightest liquid hitherto known, namely, marsh gas, whose density is  $0\cdot 4$ . It is sixteen times lighter than an equal volume of liquid oxygen, or in other words the two bodies show a greater difference in density than water and mercury. The boiling points and densities are as follows :—

Gas.	Boiling Point.	Liquid Density at the Boiling Point.
Oxygen . . .	$- 182^{\circ}\cdot 5$ C.	$1\cdot 13$
Nitrogen . . .	$- 195^{\circ}\cdot 6$ C.	$0\cdot 80$
Hydrogen . . .	$- 252^{\circ}\cdot 3$ C.	$0\cdot 07$

In my experiments with helium in 1901, it was expanded adiabatically, using the Cailletet method, from a pressure of 100 atmospheres at the temperature of solid hydrogen down to one atmosphere, without showing any temporary mist during expansion, from which it was inferred that the gas had been cooled to at least  $9^{\circ}$  and still no liquefaction had occurred. Similar experiments were made by Olszewski in 1905, and he has expressed the view that helium may be practically a permanent gas which we should hardly ever succeed in liquefying. Without offering any opinion other than what I have already expressed as to the probability of helium being liquefiable, let us study the application of the method to helium which was found successful with hydrogen. This method, first used technically by Linde, consisted in the use of a regenerative circuit along with expansion through a fine nozzle (pin-hole).

A pipe fixed in the King's Well at Bath enabled the escaping gas to be collected and sent to London. This gas consists almost entirely of nitrogen, but contains about one two-thousandth part of its volume of helium—in other words, 2000 cubic feet of the gas would contain 1 cubic foot of helium. The helium was concentrated from the crude gas by partially liquefying out the nitrogen, marsh gas and other impurities until it contained only about 30 per cent. of nitrogen along with helium and neon. In this condition it was put through the regenerative circuit under a pressure of about 100 atmospheres, yielding a quantity of liquid nitrogen, which was removed. The nitrogen remaining in the helium mixture had now fallen to 5 per cent., and on continuing to circulate the regenerator tubes got plugged with solid. To the helium gas, which was now too small a quantity to circulate well, was added 25 per cent. of hydrogen, and this mixture, on circulating, froze also in the regenerator tubes. A further addition of hydrogen, up to 50 per cent., was made to the gas, which after passing through the regenerating circuit, gave a

considerable amount of solid on the external coil, and finally the internal tubes plugged. During the evaporation of the solid deposited on the coil in the fourth circulation, the composition of the gases given off in three successive portions were as follows :—

—	First	Second	Third
Hydrogen . . .	41·0	37·0	34·8
Nitrogen . . .	5·2	16·4	48·0
Helium and Neon .	53·8	46·6	17·2
	100·0	100·0	100·0

The gas analysis suggests that the solid was composed of a mixture of solid hydrogen and nitrogen along with dissolved helium and neon.

The gaseous portion remaining after the last circulation, on being freed from hydrogen, consisted of 94 per cent. of helium and 6 per cent. of neon. To this helium and neon 75 per cent. of hydrogen was added, which, on passing round the regenerative circuit, yielded liquid hydrogen containing 13 per cent. of helium in solution, along with some solid presumably neon in the bottom of the vacuum vessel. The final helium left uncondensed in the circuit after the removal of the hydrogen contained 4 per cent. of neon.

Now how could the hydrogen be frozen during the circulation of the helium and hydrogen mixture? An experiment made on a former Friday evening with nitrogen will explain. On that occasion hydrogen was allowed to bubble up through a quantity of liquid nitrogen. The bubbles, in accordance with Dalton's law, being free of nitrogen induce a rapid evaporation of the liquid nitrogen into them as they pass through it, thus causing cooling, until the liquid nitrogen becomes first viscous and finally freezes into a jelly containing spiral tubes through which the hydrogen escapes. In the same way the passage of the uncondensed helium through or over liquefied hydrogen formed by spray on the regenerator coils lowers its temperature and finally causes it to freeze.

Such regenerative operations were carried on under considerable difficulties as it was impossible to see properly what was taking place in the apparatus, and at any moment the vacuum vessels might collapse. On one occasion, the whole of the helium that had been accumulated during 2 years was lost owing to the collapse of the glass vacuum vessel containing the regenerator coil, and the experiment of accumulating helium had to begin *de novo*.

The use of charcoal provides us with a ready means of studying the properties of gas mixtures containing helium. A sparking-tube, having a branch charcoal bulb attached, was charged with Bath-gas.



On immersing the charcoal bulb in liquid air, the nitrogen was rapidly absorbed and the discharge finally was that due to helium and neon. Now the helium spectrum contains two very prominent lines, one in the yellow and one in the green, and at very low pressures the green predominates. In another tube, the initial pressure was considerably reduced, and the green coloration was very strikingly displayed.

The intense red colour given out by neon vacuum tubes is now well known. On immersing one end of such a neon tube in liquid hydrogen, the gas was immediately differentiated, the more condensable and heavier neon sinking to the lower end of the tube, where it revealed itself by its orange-ruddy glow, while the upper end of the tube retained the yellow colour of the helium discharge, thus demonstrating that the gas in the tube was a mixture of helium and neon.

VELOCITY OF ABSORPTION OF AIR BY CHARCOAL AT  $-185^{\circ}\text{C}$ .  
UNDER SMALL PRESSURES.

For this purpose a long horizontal glass tube, A, Plate I., over an inch in diameter having either platinum electrodes sealed in at the ends or external tin foil electrodes, had a charcoal condenser immersed in liquid air attached, B, together with a means, after the vacuum was so high that no discharge would pass, of allowing a definite small volume of dry air to enter between two stop-cocks C. On opening the stop-cock D to the charcoal condenser, rapid exhaustion took place, which was measured at definite periods, after shutting off the charcoal, by the McLeod gauge E, which had no india-rubber joints or tubes used in its construction.

In the course of observations in high vacua it was found that metallic electrodes are unreliable because they occlude gas. For this reason, therefore, it was necessary to work with external tin-foil electrodes.

The rate of exhaustion may be gathered from the fact that 20 grammes of charcoal cooled in liquid air was able to reduce the pres-

Time of Exhaustion.	Pressure in mm.	Time of Exhaustion.	Pressure in mm.
0 sec.	2.190	60 sec.	0.347
10 "	1.271	2 min.	0.153
20 "	0.869	5 "	0.0274
30 "	0.632	10 "	0.00205
40 "	0.543	19 "	0.00025
50 "	0.435		

sure of air in the tube of 2000 c.c. capacity from one three-hundred-and-fiftieth of an atmosphere to one three-millionth of an atmosphere

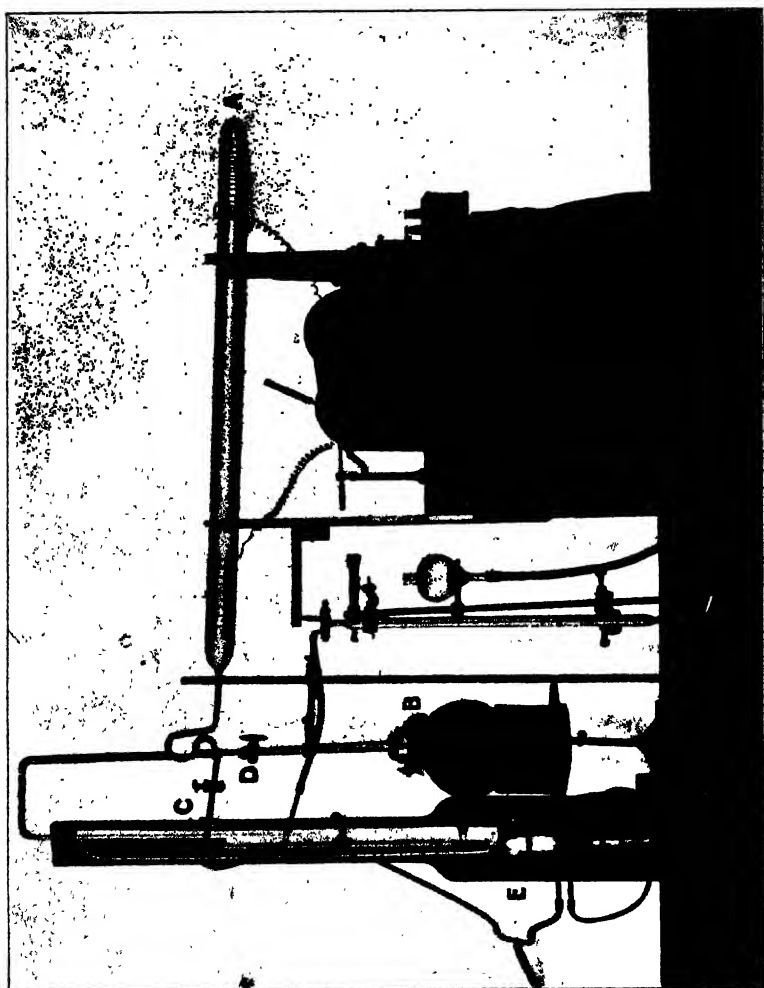
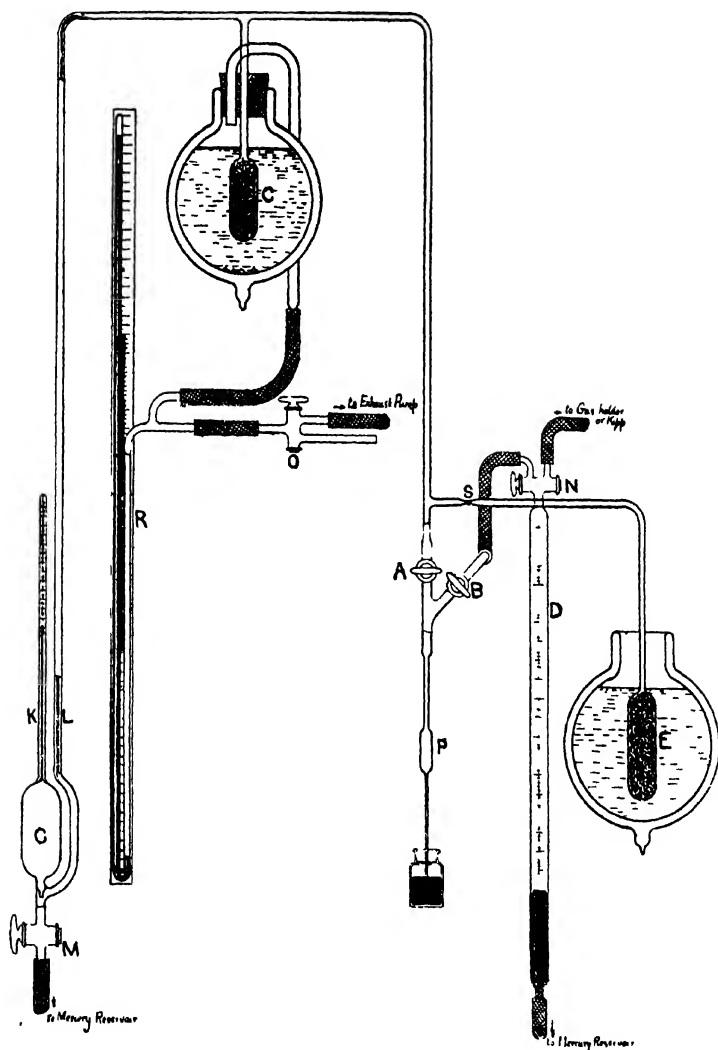


PLATE II.



in 19 minutes. The annexed table gives the observations. The law connecting pressure and time in this particular apparatus seems to be given by a formula of the type

$$\log\left(\frac{a}{t}\right) \log\left(\frac{b}{p}\right) = c$$

where  $t$  and  $p$  are time and pressure, and  $a$   $b$   $c$  are constants.

#### CHARCOAL OCCLUSION PRESSURES OF HYDROGEN AND NITROGEN.

The apparatus sketched in Plate II., illustrates how the gas concentration, pressure and temperature are measured. The mass of charcoal E, immersed in liquid air, is used for the preliminary exhaustion of the McLeod gauge G, and the charcoal in C to be used in the experiments, and is then sealed off at S. Afterwards the bulb C is placed in a large spherical vacuum flask containing liquid oxygen which can be made to boil at any definite temperature under diminished pressure measured on the manometer R. The volume of gas admitted into the charcoal is measured by the burette D and pipette P and the corresponding occlusion pressure at any concentration and temperature below that of 90° abs., by the gauge G.

For small concentrations the relation between the pressure and the concentration of different gases in presence of charcoal, shows very great variation, all being at the same temperature. The following table gives the comparison between hydrogen and nitrogen at the temperature of liquid air, 25 grammes of charcoal being used.

Volume of Gas Absorbed.	Occlusion Hydrogen Pressure.	Occlusion Nitrogen Pressure.
c.c.	mm.	mm.
0	0·00003	0·00005
5	0·0228	..
10	0·0455	..
15	0·0645	..
20	0·0861	..
25	0·1105	..
30	0·1399	0·00031
35	0·1623	..
40	0·1870	..
190	..	0·00110
500	..	0·00314
1000	..	0·01756
1500	..	0·02920
2500	..	0·06172

Hence we see that 15 c.c. of hydrogen produced nearly the same pressure (0·0645 mm.) as 2500 c.c. of nitrogen (its pressure being

0.06172 mm.). This shows how different the occlusion volatility of hydrogen is at the temperature of liquid air as compared with that of nitrogen for equal concentration. In a corresponding manner the concentrations, for the same pressure, vary greatly with the temperature. The following table exemplifies this, even although the pressures are not quite constant.

Gas.	Concentration in c.c. per grm. of Charcoal.	Pressure in mm.	Temperature Absolute.
Helium . . .	97	2.2	20°
Hydrogen . . .	397	2.2	20°
Hydrogen . . .	15	2.1	90°
Nitrogen . . .	250	1.6	90°
Oxygen . . .	300	1.0	90°
Carbon dioxide . . .	90	3.6	195°

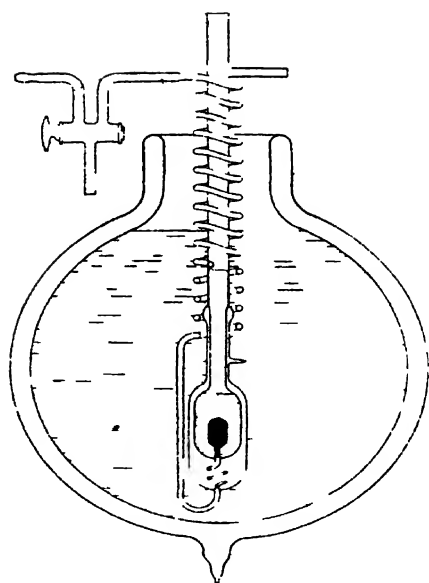
The temperatures employed were the boiling-points of hydrogen, oxygen, and carbon dioxide.

#### THE HEAT OF OCCLUSION FOR DIFFERENT GASES IN CHARCOAL.

Accompanying the condensation of all gases to the liquid state there is evolution of heat, and we know that during the absorption of a gas in charcoal, or any other occluding body; as for instance, the occlusion of hydrogen in palladium; the amount generated exceeds that of direct liquefaction. From the relation between occlusion pressure and temperature at the same concentration, the reaction being reversible, we are able to calculate this heat-evolution. Thus, if the concentration in the charcoal for each of the following gases has the values given in the table, then the following mean molecular latent heats of occlusion result from my experiments.

Gas	Concentration c.c. per grm.	Molecular Latent Heat	Mean abs Temperature.
	c.c.		°
Helium . . .	97	483.0	18
Hydrogen . . .	390	524.4	18
Hydrogen . . .	20	2005.6	78
Nitrogen . . .	250	3059.0	82
Oxygen . . .	300	3146.4	82
Carbon dioxide . . .	90	6099.6	180

The concentrations of the occluded gases were so regulated as to start with an initial pressure not exceeding 3 mm. at the respective boiling-points of hydrogen, nitrogen, oxygen, or carbonic acid.



A liquid air calorimeter such as I have described in former lectures\* was modified so as to make a direct determination possible of the heat evolved during charcoal absorption at low temperatures. The apparatus will easily be understood from the drawing (Plate III.). The value of hydrogen absorption per molecule found by this method was 1940 calories, which is of the same order of magnitude as that which resulted from the occlusion pressure observations taken a little below the boiling point of liquid air.

#### RADIOMETER STUDIES.

No instrument is more convenient for the demonstration of the high vacuum produced by cooled charcoal than the radiometer of Sir William Crookes. A convenient arrangement of the attached charcoal tube is shown in Plate IV., Fig. 3. In order to wash out the radiometers, it was found that a bulb containing perchlorate of potash was the most reliable source of pure oxygen, and when the gases from minerals have to be examined a side tube must be added. The general arrangement is shown in Plate IV., Fig. 2, where A is the perchlorate bulb and E the side tube.

#### HELIUM RADIOMETER.

A Crookes radiometer, filled with helium, having a glass tube ending in a bulb containing charcoal, remained inactive to the concentrated beam of the electric arc after the charcoal was cooled in liquid air, but on replacing the liquid air by liquid hydrogen the radiometer vanes began to spin with great rapidity.

On further reducing the temperature by exhausting the hydrogen till it froze, the rotation seemed to be but little altered. This final drop in temperature to  $14^{\circ}$  absolute without much change in the motion indicated that there was still a considerable gas pressure left, from which we infer, by analogy with other gases, that the freezing point of hydrogen is still very much higher than the boiling-point of helium.

#### HYDROGEN RADIOMETER.

A Crookes radiometer was filled with hydrogen instead of helium. When the charcoal bulb attached to this radiometer was immersed in liquid air, and the beam from the electric arc was focused on the vanes, rotation took place. This corresponded with what happened when the charcoal bulb of the helium radiometer was immersed in liquid or solid hydrogen; in both cases the cooling had rarefied the gases sufficiently to permit motion. But, on allowing the vanes of the hydrogen radiometer to come to rest, and immersing its charcoal

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\* Roy. Inst. Proc., 1894, vol. xiv. p. 398, and 1904, vol. xvii. p. 581.

bulb in liquid hydrogen for only half a minute, the rarefaction became so great that, when the arc light was thrown on, the vanes remained perfectly still. From a comparison of these two experiments we may again derive an indication of the boiling-point of helium. For, in the case of the hydrogen radiometer, a fall of 75 per cent. in the temperature of the charcoal bulb, from the boiling-point of air to the boiling-point of hydrogen, reduced the vanes to rest; similarly, we may infer that a fall of like amount from the boiling-point of hydrogen would reduce the vanes of the helium radiometer to rest, a result which would make the boiling-point of helium about  $5^{\circ}$  or  $6^{\circ}$  absolute, as before.

A variation of the hydrogen radiometer experiment may be made as follows. Into the bulb of the radiometer a branch tube was sealed containing a little metallic sodium. On immersing the charcoal bulb in liquid hydrogen, and throwing on the electric beam, the vanes remained at rest as before; but on gently heating the sodium, a minute quantity of hydrogen was liberated which was sufficient to re-start the radiometer for a short period of time. In a few minutes, however, the absorption of hydrogen by the charcoal became so efficient that the radiometer stopped.

#### ORDINARY AIR RADIOMETER.

A radiometer, with attached charcoal bulb, was repeatedly washed out with the oxygen and nitrogen vapour coming from old liquid air, and sealed off at a pressure of a fraction of about a millimetre of mercury. On immersion of the charcoal tube in liquid air, the motion of the vanes did not cease, but, on immersion in liquid hydrogen, a minute or two sufficed to bring the motion completely to a stop. The explanation of the experiment is that old liquid air is not a mixture of oxygen with a small proportion of nitrogen and argon, but it always contains traces of neon and helium.

#### OXYGEN AND NITROGEN RADIOMETER.

The effect of the residual gases contained in air can be shown as follows: The bulb of a Crookes radiometer was thoroughly washed out with a mixture of pure chemical oxygen, care being taken that no hydrogen, neon or helium was present. This bulb was not provided with a side charcoal tube, but had a long quill tube attached, a few inches of which could be cooled in liquid hydrogen. The radiometer, thus charged with pure oxygen, had a portion of the quill tube cooled in liquid hydrogen. The motion entirely ceased through the condensation and solidification of the gas at  $20^{\circ}$  Abs. When air was used instead of the chemically prepared oxygen, the same radiometer was not stopped owing to the presence of helium and neon in the atmosphere.



Fig 3

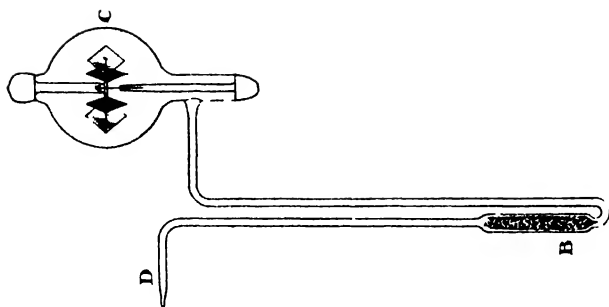


Fig 2

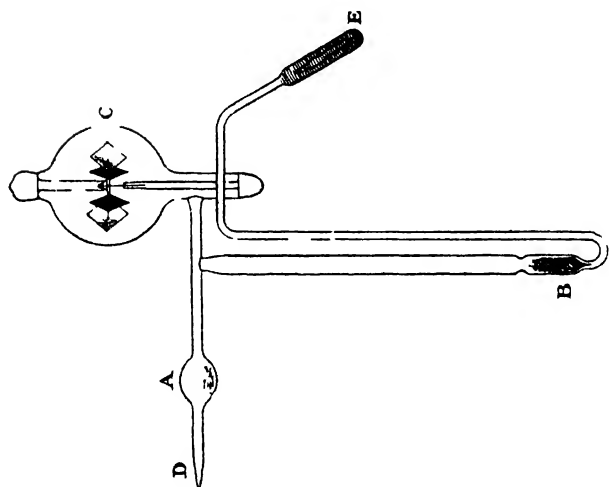
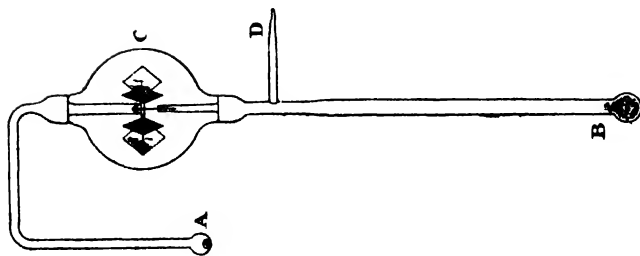


Fig 1



## THORIANITE.

The rare substance, thorianite, when heated gives off helium. Advantage of this was taken in the following experiment: A Crookes radiometer, with the usual tube of charcoal attached, was provided with an additional tube containing a small crystal of thorianite. On immersing the charcoal bulb in liquid hydrogen and throwing on the electric beam, no motion took place. The thorianite was, in these circumstances, heated by the flame of a Bunsen burner, and immediately supplied enough helium to set the vanes in motion, and the instrument remained active in spite of prolonged cooling of the charcoal with liquid hydrogen.

## ELECTRIC DISCHARGE RADIOMETER.

All the previous radiometers used were of the ordinary Crookes pattern in which the mica vanes were blackened on one side. In the experiment about to be described, a radiometer, with the usual charcoal tube attached, was employed; but it differed from the ordinary radiometer in that the one side of each vane was covered with a thin sheet of aluminium. The metallic frame bearing the vanes was connected to one of the terminals of an induction coil, and the other to a pole sealed through the glass of the radiometer. The bulb, therefore, was a kind of discharge-tube containing a light mill. On turning on the current, the vanes being made the negative pole, the bulb lit up with a fine luminescence, and began to rotate rapidly. But on immersing the charcoal bulb in liquid air, the vacuum was greatly intensified, the glow became much diminished, and the rotation of the vanes ceased altogether; even the additional stimulus of the beam from the electric arc was insufficient to produce any motion.

EXPERIMENT WITH MERCURY VAPOUR TO MEASURE PRESSURE  
IN A RADIOMETER.

During the experiments on high vacua it became abundantly evident that the pressures reached were difficult to determine by means of the McLeod gauge. Minute quantities of helium were to be found everywhere—in the atmosphere, in the fine films of gases condensed on the surfaces of glass vessels, on vanes and elsewhere. It became, therefore, of importance to determine very small pressures by other means, if possible. The radiometer experiments suggested such a means, namely, by determining pressures below which the radiometer would not spin. The pressures of mercury vapour have been very accurately determined throughout a wide range of temperature. The following experiment shows how such measures can be used to ascertain the limit of pressure referred to above. A Crookes

radiometer (Plate IV., Fig. 1), with its attached charcoal bulb B, had sealed on to it a tube ending in a small bulb A containing a globule of mercury. The radiometer and charcoal bulb had previously been heated, exhausted, and repeatedly washed out with pure oxygen gas, and the mercury allowed to distil for some time into the charcoal cooled in liquid air. On exposing the radiometer to the electric beam the vanes began to spin. On cooling the mercury bulb in liquid air, the radiometer soon became inactive; but on replacing the liquid air by ordinary water, as the temperature rose, the mercury began to evaporate and the radiometer resumed its activity. It was found that the particular radiometer used became active when the temperature of the mercury had risen to  $-23^{\circ}\text{C.}$ , which corresponded to a pressure of about a fifty-millionth of an atmosphere. As an example of the limits to which charcoal exhaustion extends, the following table gives the pressures obtained by the use of 5 grammes of charcoal attached to a bulb of 300 c.c. capacity containing air at an initial pressure of about 1.7 mm. and at the temperature of  $15^{\circ}\text{C.}$

Time of Exhaustion				Pressures in mm.
0 minutes	in liquid air	.	.	1.6845
5	"	"	.	0.0545
10	"	"	.	0.01032
30	"	"	.	0.000139
60	"	"	.	0.000047
10	"	"	hydrogen	0.0000154
10	"	solid	"	0.0000058

Thus from an initial pressure of  $\frac{1}{330}$  of an atmosphere, the pressure could be reduced to one 130-millionth of an atmosphere.

[J.D.]

Friday, January 17, 1908.

GEORGE MATTHEY, Esq., F.R.S., Manager, in the Chair.

Professor T. E. THORPE, C.B. PH.D. LL.D. D.Sc. F.R.S. *M.R.I.*

*The Centenary of Davy's Discovery of the Metals of  
the Alkalies.*

A HUNDRED years ago last October, there happened one of those events to which the term epoch-making may, without cavil or question, be fittingly applied.

As it was an occurrence with which the name and fame of the Royal Institution are inseparably bound up, the Managers have thought it only proper that its centenary should not pass unnoticed here, and it is by their wish, therefore, that I appear on this the first possible opportunity after the actual date of its hundredth anniversary to give you some account of it, and to state, so far as I am able and within the limits of an hour, the fruitful consequences that have flowed from it.

Let me, in the first place, attempt to recall the circumstances which led up to that cardinal discovery of which to-night we celebrate the centenary. These are connected partly with the Institution itself, and partly with the state of science in the early years of the 19th century.

In the year 1807 this Institution was entering upon the eighth year of its existence. As you doubtless know, the Royal Institution grew out of a proposal to deal with the question of the unemployed—namely, by forming in London by private subscription an establishment for feeding the poor and giving them useful employment, and also for furnishing food at a cheap rate to others who may stand in need of such assistance, connected with an institution for introducing and bringing forward into general use new inventions and improvements, particularly such as relate to the management of heat and the saving of fuel, and to various other mechanical contrivances by which domestic comfort and economy may be promoted. Such was the original prospectus, but, like many other prospectuses, it failed to equal the promise its projectors held out.

Eventually the promoters decided, on the initiation of Count Rumford, that the Associated Institution would, as they expressed it, be “too conspicuous and too interesting and important, to be made an *appendix* to any other existing establishment,” and therefore it ought to stand alone, on its own proper basis.

Accordingly the problem of the unemployed still remains with us, whilst the new institution took the form of converting Mr. Mellish's house in Albemarle Street into a place where, by regular courses of philosophical lectures and experiments, the applications of the new discoveries in science to the improvement of the arts and manufactures might be taught, so as to facilitate the means of procuring the comforts and conveniences of life.

The Royal Institution had a troubled infancy. Like the poor it was originally designed to succour, it suffered much in the outset from lack of nourishment. To add to its miseries, the little starveling was caricatured by Gillray, lampooned by Peter Pindar, and ridiculed by Lord Brougham; and it was literally in the throes of dissolution when new life was breathed into it by the opportune arrival, in 1801, of a small spare youth of 22, from Bristol, whom the Managers had engaged at a salary of 100 guineas a year. The youth was Humphry Davy, who had acted as assistant to Dr. Beddoes, of the Pneumatic Institution, and who had already made some slight stir in scientific circles by his discovery of a characteristic property of nitrous oxide. In announcing his arrival to the Managers, Count Rumford reported that he had purchased a cheap second-hand carpet for Mr. Davy's room, together with such other articles as appeared to him necessary to make the room habitable, and among the rest a new sofa-bed, which, in order that it may serve as a model for imitation, had been made complete in all its parts. Six weeks after his arrival Davy was called upon to lecture, and a descriptive paragraph of the period thus chronicles his success in the *Philosophical Magazine* for 1801:—

"It must give pleasure to our readers to learn that this new and useful institution, the object of which is the application of Science to the common purposes of life, may be now considered as settled on a firm basis. . . .

"We have also to notice a course of lectures, just commenced at the institution, on a new branch of philosophy—we mean the Galvanic Phenomena. On this interesting branch, Mr. Davy (late of Bristol) gave the first lecture on the 25th of April. He began with the history of Galvanism, detailed the successive discoveries, and described the different methods of accumulating galvanic influence. . . . He showed the effect of galvanism on the legs of frogs, and exhibited some interesting experiments on the galvanic effects on the solution of metals in acids. Sir Joseph Banks, Count Rumford, and other distinguished philosophers were present. The audience were highly gratified, and testified their satisfaction by general applause. Mr. Davy, who appears to be very young, acquitted himself admirably well; from the sparkling intelligence of his eye, his animated manner, and the *tout ensemble*, we have no doubt of his attaining a distinguished eminence."

And what was of more immediate consequence, this confident

assurance was shared also by the Managers, for at a subsequent meeting they unanimously resolved "that Mr. Humphry Davy, Director of the Chemical Laboratory, having given satisfactory proofs of his talents as a lecturer, should be appointed, and in future denominated, Lecturer in Chemistry at the Royal Institution, instead of continuing to occupy the place of Assistant Lecturer, which he has hitherto filled."

That such shrewd experienced men of the world as Sir Joseph Banks and Rumford, who were the moving spirits in the management of the Institution and genuinely solicitous for its welfare, should thus entrust its fortunes, then at their lowest ebb, to the power and ability of a young and comparatively unknown man, barely out of his teens, seems, even in an age which was familiar with the spectacle of "a proud boy" as a Prime Minister, like the desperate throw of a gambler.

But Banks and Rumford had, doubtless, good reason for the faith that was in them. For a happy combination of circumstances had served to bring the Cornish youth within the range of many who could be of service to him in that search for the fame for which he hungered. His connection with the Beddoes brought him the friendship of the Edgeworths, and it is amusing to trace how the good-humoured patronage of the gifted Maria quickly passed into amazement and ended in awe as her acquaintance with him ripened. Living in Bristol, he was at once brought into that remarkable literary coterie which distinguished that city at the close of the eighteenth century. Southey spoke of him as a miraculous young man, whose talents he could only wonder at. Cottle, the publisher, on one occasion said to Coleridge, "You have doubtless seen a great many of what are called the cleverest men—how do you estimate Davy in comparison with these?" Mr. Coleridge's reply was strong and expressive. "Why, Davy can eat them all! There is an energy, an elasticity, in his mind which enables him to seize on and analyse all questions, pushing them to their legitimate consequences. Every subject in Davy's mind has the principle of vitality. Living thoughts spring up like turf under his feet."

Davy's experimental work on "the pleasure-giving air" had made him known to the Watts and the Wedgewoods. Priestley, then in exile, and Hope of Edinburgh were greatly impressed with the philosophical acumen of the author of phosoxygen, and he had a powerful friend in his own countyman Davies Gilbert, who succeeded him in the Presidential Chair of the Royal Society. We need be in no doubt, therefore, as to the influences which conspired to bring Davy into what he termed "the great hot-bed of human power called London."

The mention of Davy's first course of lectures in this Institution brings me at once to the proper subject of this discourse.

The first year of the last century is memorable for the invention

of the voltaic battery and for its immediate application by Nicholson and Carlisle in this country to the electrolytic decomposition of water.

Davy himself has said, "The voltaic battery was an alarm bell to experimenters in every part of Europe; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy."

We owe it to Sir Joseph Banks that Volta's great discovery was first made known to English men of science, and the study of the phenomena of Galvanic Electricity was at once entered upon by a score of experimenters in this country. Among them was Davy. Even before he left Bristol he was hard at work on the subject, sending the results of his observations to Nicholson's *Journal* in a series of short papers. He resumed his inquiries immediately on his arrival in London, and was doubtless well prepared, therefore, for his opening course of lectures.

In 1801 he sent his first communication to the Royal Society on "An Account of Some Galvanic Combinations Formed by the Arrangement of Single Metallic Plates and Fluids, Analogous to the New Galvanic Apparatus of Mr. Volta." Although the work was continually interrupted by requests made to him by the Managers to carry out their own ideas of facilitating the means of procuring the comforts and conveniences of life, he never lost sight of the subject of voltaic electricity, and in spite of innumerable distractions due to the precarious position of the Institution, he gradually accumulated the material, out of which grew his first Bakerian Lecture "On Some Chemical Agencies of Electricity," read before the Royal Society on November 20th, 1806. I have ventured elsewhere to express my opinion of this paper. In my judgment it constitutes, in reality, Davy's greatest claim as a philosopher to our admiration and gratitude, for in it he, for the first time, succeeded in unravelling the fundamental laws of electro-chemistry, and thereby imported a new order of conceptions, altogether unlooked for and undreamt of, into science.

I am only at the moment concerned with this memoir in its relation to the discovery of which to-night we celebrate the centenary. The isolation of the metals of the alkalis was unquestionably an achievement of the highest brilliancy, and as such appeals strongly to the popular imagination. But it was only the necessary and consequential link in a chain of discovery which, had Davy neglected to make it, would have been immediately forged by another.

The publication of Davy's first Bakerian Lecture produced a great sensation, both at home and abroad. Berzelius, years afterwards, spoke of it as one of the most remarkable memoirs that had ever enriched the theory of chemistry. Very significant, too, of the

impression it made on the world of science was the action of the French Institute. Bonaparte, then First Consul, had announced his intention of founding a medal "for the best experiment which should be made in the course of each year on the galvanic fluid," and a committee of the Institute, consisting of Laplace, Halle, Coulomb, Haüy, and Biot, was appointed to consider the best means of giving effect to the wishes of the First Consul. To the young man, with the little brown head, like a boy (as Lady Brownrigg described him), now 28 years of age, was awarded the medal. All the Institute got from the founder of the medal was, what Maria Edgeworth termed, "a rating all round in imperial Billingsgate." There was no *entente cordiale* in those days; indeed, the feeling of animosity was intense. Of course, there were persons who said that patriotism should forbid the acceptance of the award. Davy's own view was more sensible and politic: "Some people," he said to his friend Poole, "say I ought not to accept this prize; and there have been foolish paragraphs in the papers to that effect; but if the two countries or governments are at war, the men of science are not. That would, indeed, be a civil war of the worst description; we should rather, through the instrumentality of men of science, soften the asperities of national hostility."

Thanks to the kindness of Dr. Humphry Davy Rolleston, the grandson of Dr. John Davy, the brother of Sir Humphry, who has also been so good as to lend me this admirable bust of the great chemist by Chantrey, and this charming portrait by Jackson, I am able to show you this evening this historically interesting medal.

What Davy looked like at this period of his life may be seen from the picture I now project upon the screen. It is a reproduction of the large portrait which hangs in the vestibule, and which the Institution owes to the thoughtful kindness of the late Mr. Graham Young.

As the applications of voltaic electricity seemed in 1806 to have no immediate bearing on the comforts and conveniences of life, Davy, during the greater part of the following year, was required to direct his attention to other matters. But in the late summer of 1807 he was able to resume his work with the voltaic battery, and he commenced to study its action on the alkalis.

That the alkalis—potash and soda—would turn out to be compound substances was not an unfamiliar idea at the time, and it is significant that almost immediately after Nicholson and Carlisle had resolved water into its elements by the action of voltaic electricity, Henry, of Manchester, the friend and collaborator of Dalton, should have made the attempt to apply the same agency to the separation of the presumed metallic principle of potash. The conception that what the older chemists called "earths" might be made to yield metals was at least as old as the time of Boyle, and probably dates back from the earliest days of alchemy. The relation of the earths to the metals was part of the doctrine of Becher and Stahl: it was no less a



part of the antiphlogistic doctrine of Lavoisier, although the points of view were diametrically opposed. Neumann attempted to obtain a metal from lime, Bergman considered that baryta was, like lime, a metallic calx, and Baron that alumina contained a metal. From their many analogies to these substances it was not unreasonable, therefore, to surmise that potash and soda might also contain metallic principles.

I have elsewhere pointed out that there is some evidence that whilst at Bristol Davy had already attacked the problem of the resolution of the alkalis by means of voltaic electricity. What precise idea he had in again attacking it, or what expectation he had of a definite result, is difficult to determine. In one of his lectures on Electro-chemical Science, delivered some time subsequently, he said he had a suspicion at the time that potash might turn out to be "phosphorus or sulphur united to nitrogen," conceiving, that as the volatile alkali was composed of the light inflammable hydrogen united to nitrogen, so the fixed and denser alkalis might be composed of the denser inflammable bodies—phosphorus and sulphur—also united to nitrogen.

Davy once said that "analogy was the fruitful parent of error," and few more striking instances of perverted analogy are to be met with in science than this. In another of his lectures he said of the alchemists that "even their *failures* developed some unsought-for object partaking of the marvellous"; and if such had been his reasoning, the statement is no less true of himself.

So far as can be ascertained, it was on October 19, 1807, that he obtained his first decisive result. This is thus described in Davy's own handwriting in the Laboratory Journal, which has been preserved for us by the pious care of Faraday, and which is one of the most precious of the historical possessions of the Royal Institution: "When potash was introduced into a tube having a platina wire attached to it, so [fig.], and fused into the tube so as to be a conductor—i.e. so as to contain just water enough, though solid—and inserted over mercury, when the platina was made negative, no gas was formed and the mercury became oxydated, and a small quantity of the alkaligen was produced round the platina wire, as was evident from its quick inflammation by the action of water. When the mercury was made the negative, gas was developed in great quantities from the positive wire, and none from the negative mercury, and this gas proved to be pure oxygen—a capital experiment, proving the decomposition of potash."

On the 19th of the following month he delivered what is generally regarded as the most memorable of all his Bakerian Lectures. It is entitled "On some New Phenomena of Chemical Changes produced by Electricity, particularly the Decomposition of the fixed Alkalies; and the Exhibition of the new substances which constitute their bases; and on the general Nature of Alkaline Bodies."

Few discoveries of like magnitude have been made and perfected in so short a time, and few memoirs have been more momentous in result than that which, put together in a few hours, gave the results of that discovery to the world.

The whole work was done under conditions of great mental excitement. His cousin, Edmund Davy, who at the time acted as his assistant, relates that when he saw the minute globules of the quicksilver-like metal burst through the crust of potash and take fire, his joy knew no bounds; he actually danced about the room in ecstasy, and it was some time before he was sufficiently composed to continue his experiments.

The rapidity with which he accumulated results, after this first feeling of delirious delight had passed, was extraordinary, and he had obtained most of the leading facts concerning the physics and chemistry of the new substances before the middle of November.

He began his lecture with a felicitous reference to the concluding remarks of one of the previous year, namely: "That the new methods of investigation promised to lead to a more intimate knowledge than had hitherto been obtained concerning the true elements of bodies. This conjecture, then sanctioned only by strong analogies, I am now happy to be able to support by some conclusive facts."

In the first attempts he made to decompose the fixed alkalis he acted upon concentrated aqueous solutions of potash and soda with the highest electrical power he could then command at the Royal Institution, viz., from voltaic batteries containing 23 plates of copper and zinc of 12 inches square, 100 plates of 6 inches, and 150 of 4 inches, charged with solutions of alum and nitric acid; but although there was high intensity of action, nothing but hydrogen and oxygen was disengaged. He next tried potash in igneous fusion, and here the results were more encouraging: there were obvious and striking signs of decomposition; combustible matter was produced, accompanied with flame and a most intense light. He had observed that, although potash, when dry, is a non-conductor, it readily conducts when it becomes damp by exposure to air, and in this state "fuses and decomposes by strong electrical powers."

Let me state in his own words, for the words are classical, what followed:—

"A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conductive power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4 [that is 100 plates of 6 inches square and 150 plates of 4 inches square] in a state of intense activity; and a platina wire communicating with the positive side was brought in contact with the upper surface of the alkali . . . . Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the

lower, or negative surface, there was no liberation of elastic fluid ; but small globules, having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces."

He goes on to say :—

"Soda, when acted upon in the same manner as potash, exhibited an analogous result ; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces.

"The substance produced from potash remained fluid at the temperature of the atmosphere at the time of its production ; that from soda, which was fluid in the degree of heat of the alkali during its formation, became solid on cooling, and appeared having the lustre of silver."

It would seem from this description of its properties that the potassium Davy first obtained was alloyed with sodium owing to the fact that the potash contained soda. Potassium is solid up to 143° F., whereas, as Davy was the first to show, an alloy of potassium and sodium is fluid at ordinary temperatures.

On account of their alterability in contact with air, Davy had considerable difficulty in preserving and confining the new substances so as to examine their properties. As he says, like the Alkahests imagined by the Alchemists, they acted more or less upon almost every body to which they were exposed. Eventually, he found they might be preserved in mineral naphtha.

The "basis" of potash was described by him as a soft malleable solid with the lustre of polished silver.

"At about the freezing point of water it becomes harder and brittle, and when broken in fragments, exhibits a crystallised texture which in the microscope seems composed of beautiful facets of a perfect whiteness and high metallic splendour. It may be converted into vapour below a red heat, and may be distilled unchanged, and is a perfect conductor of heat and electricity. Its most marked difference from the common run of metals is its extraordinary low specific gravity." At the time of its discovery, it was the lightest solid known.

The "basis" of soda was found to have somewhat similar properties. It was slightly heavier than the "basis" of potash, and fused at a higher temperature.

Davy next examined the behaviour of the new substances towards a large number of reagents, but as his observations are now the common property of the text-books, it is unnecessary here to dwell upon them.

He then enters upon some general observations on the relations of the "bases" of potash and soda to other bodies :

"Should the bases of potash and soda be called metals? The greater number of philosophical persons," he says, "to whom this question has been put, have answered in the affirmative. They agree with metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination.

"Their low specific gravity does not appear a sufficient reason for making them a new class; for amongst the metals themselves there are remarkable differences in this respect. . . . In the philosophical division of the classes of bodies, the analogy between the greater number of properties must always be the foundation of arrangement.

"On this idea, in naming the bases of potash and soda, it will be proper to adopt the termination which by common consent has been applied to other newly discovered metals, and which, though originally Latin, is now naturalised in our language.

"Potassium (*sic*) and sodium are the names by which I have ventured to call the new substances; and whatever changes of theory, with regard to the composition of bodies, may hereafter take place, these terms can scarcely express an error; for they may be considered as implying simply the metals produced from potash and soda. I have consulted with many of the most eminent scientific persons in this country upon the methods of derivation, and the one I have adopted has been the one most generally approved. It is perhaps more significant than elegant. But it was not possible to find names upon specific properties not common to both; and though a name for the basis of soda might have been borrowed from the Greek, yet an analogous one could not have been applied to that of potash, for the ancients do not seem to have distinguished between the two alkalies."

Such, then, are the more significant features of one of the greatest discoveries ever made by a British chemist, as these are set forth in one of the most remarkable papers in the Philosophical Transactions of the Royal Society.

Sir James Dewar has been so good as to have prepared for me a photographic reproduction of a water-colour drawing of the laboratory of the Royal Institution as it existed in Davy's time, showing the actual spot where the isolation of the metals of the alkalis was first effected.

The publication of Davy's discovery created an extraordinary sensation throughout the civilised world, a sensation not less profound, and certainly more general from its very nature, than that which attended his lecture of the previous year. But at the very moment of his triumph, it seemed that the noise of the universal acclaim with which it was received was not to reach him. I have already made reference to the condition of mental excitement under which the discovery was made and prosecuted. Almost immediately after the delivery of his lecture he collapsed, struck down by an illness which nearly proved fatal, and for weeks his life hung on a

thread. He had been in a low feverish condition for some time previously, and a great dread had fallen upon him that he should die before he had completed his discoveries. It was in this condition of body and mind that he had applied himself to the task of putting together an account of his results. Four days after this was given to the world he took to his bed, and he remained there for nine weeks. Such a blow following hard on the heels of such a triumph aroused the liveliest sympathy. The doors of the Royal Institution were beset by anxious inquirers, and written reports of his condition at various periods of the day had to be posted in the hall. The strength of the feeling may be gleaned, too, from the sentences with which the Rev. Dr. Dibdin, who had been hurriedly engaged to take his place in the theatre, began the lecture introductory to the Session of 1808.

"The Managers of this Institution have requested me to impart to you that intelligence, which no one who is alive to the best feelings of human nature can hear without the mixed emotion of sorrow and delight.

"Mr. Davy, whose frequent and powerful addresses from this place, supported by his ingenious experiments, have been so long and so well known to you, has, for the last five weeks, been struggling between life and death. The effects of these experiments recently made in illustration of his late splendid discovery, added to consequent bodily weakness, brought on a fever so violent as to threaten the extinction of life. Over him it might emphatically be said in the language of our immortal Milton, that

' . . . Death his dart  
Shook, but delayed to strike.'

"If it had pleased Providence to deprive the world of all further benefit from his original talents and intense application, there has certainly been sufficient already effected by him to entitle him to be classed among the brightest scientific luminaries of his country."

After having, "at the particular request of the Managers," given an outline of Davy's investigations, Dr. Dibdin proceeded to say:—

"These may justly be placed among the most brilliant and valuable discoveries which have ever been made in chemistry, for a great chasm in the chemical system has been filled up; a blaze of light has been diffused over that part which before was utterly dark; and new views have been opened, so numerous and interesting, that the more any man who is versed in chemistry reflects on them, the more he finds to admire and heighten his expectation of future important results.

"Mr. Davy's name, in consequence of these discoveries, will be always recorded in the annals of science amongst those of the most illustrious philosophers of his time. His country, with reason, will be proud of him, and it is no small honour to the Royal Institu-

tion that these great discoveries have been made within its walls—in that laboratory, and by those instruments which, from the zeal of promoting useful knowledge, have, with so much propriety, been placed at the disposal and for the use of its most excellent professor of chemistry.”

And now, in the few minutes that remain to me, let me indicate what has been the outcome of this great and fundamental discovery. How far has the expectation of future important results been realised? Have sodium and potassium at all justified the hope that they would facilitate the means of procuring the comforts and conveniences of life?

I have not the time, even if I had the intention, to attempt to follow the many changes in the metallurgy of the metals of the alkalis of the past century. Let me at once proceed to show how the matter stands at the end of a hundred years.

The general properties and chemical activities of potassium and sodium are so very similar that as a matter of commercial production that metal which can be most economically obtained is necessarily the one most largely manufactured, and of the two that metal is sodium. To-day, sodium is made by thousands of tons, and by a process which in principle is identical with that by which it was first made by Davy, i.e. by the electrolysis of fused caustic soda. It is very significant that after a series of revolutions in its manufacture, sodium, having been produced from time to time on a manufacturing scale by a variety of metallurgical methods involving purely thermal processes of reduction and distillation, entirely dissociated from electricity, we should have now got back to the very principle of the process which first brought the metal to light. And that this has been industrially possible is entirely owing to another of Davy's discoveries—possibly indeed the greatest of them all—Michael Faraday. As we all gratefully acknowledge, it is to the genius and labours of Faraday—Davy's successor in this place—that the astonishing development of the application of electrical energy which characterises this age has taken its rise.

The modern method of production of sodium is based, therefore, as regards principles upon the conjoint labours of Davy and Faraday.

These principles took their present form of application at the hands of a remarkably talented American—Mr. Hamilton Y. Castner—whose too early death, in the full vigour of his intellectual powers, was an incalculable loss to metallurgical chemistry. It is by Castner's process that all the sodium of to-day is manufactured.

In the Castner process melted caustic soda produced by the electrolysis of a solution of common salt by a method also devised by Castner, is brought into an iron vessel shaped like a large cauldron, mounted in brickwork, and provided with an extension adapted to receive the negative electrode. Suspended directly above the cathode is an iron vessel attached to a lid; to its lower edge is secured iron

wire gauze, which, when the receptacle is in position, completely surrounds the cathode. The positive electrode is connected with the lid of the vessel, which is provided with openings for the escape of the gases resulting from the electrolysis, and is suitably insulated.

As the electrolysis proceeds the alkali metal, being much lighter than the molten caustic, rises from the negative electrode and passes into the receiver, the gases escaping around the edges of the cover. The molten metal collects on the surface of the caustic, and is removed by means of a large perforated spoon, the perforations enabling the melted caustic to flow out, while the metal remains in the spoon. As the several vessels are thus skimmed in succession the fused sodium is collected into an iron vessel, whence it is poured into moulds in which it congeals, forming blocks of the size and shape of an ordinary building brick. These, after being trimmed to remove adherent oxide, are immersed in paraffin oil, and are then packed into large iron drums holding about 6 or 7 cwt., capable of being closed air-tight, and protected in transit by an outer casing of wood.

The due regulation of the volume and intensity of the current is a matter of the greatest importance in order to obtain the most economical yield of the metal. No very high temperature is needed; indeed, the temperature of the fused caustic soda should not be much higher than that of its melting point. By suitably regulating the current, the soda, in fact, may be maintained at the proper temperature and in the proper degree of fluidity without extraneous heat. Fresh melted caustic soda is added to the vessel from time to time to replace the metal removed, and in this manner the process is made continuous.

The Castner process is now worked in England at Wallsend-on-Tyne, and at Weston Point, in Cheshire; at Rheinfelden, in Germany; at Clavaux, in France; also in Switzerland, and at Niagara, in America. The present yearly output amounts to about 5000 tons, but the plant already laid down is capable of producing at least twice this quantity.

The greater quantity of the sodium made in England is sent to Glasgow, where it is converted into sodium cyanide by the Cassel Cyanide Company for use in the extraction of gold. As gold is, I suppose, generally considered the principal material factor in procuring the comforts and conveniences of life, Davy's great discovery may be thus said to have secured the primary object which the projectors of the Royal Institution had in view. Other important uses of sodium are in the manufacture of peroxide for bleaching purposes, of artificial indigo, and of a number of other synthetic dye stuffs and of drugs like antipyrin.

It need hardly be said that this extraordinary development of the manufacture has not been without its influence on the price of sodium. A quarter of a century ago it was a comparatively rare metal, and a stick of it was regarded as a chemical curiosity, to be

handled with circumspection and care. Even as late as 1890 its selling price was as high as 8s. per lb. To-day it is 8d. Sodium now takes rank, therefore, with zinc, tin, copper, or aluminium as a common, ordinary metal of commerce.

I am indebted to the directors of the Castner-Kellner Company, and in particular to my friends Sir Henry Roscoe and Mr. Beilby, for affording me the opportunity, in connection with this lecture, of actually witnessing the modern process of manufacturing sodium as it is carried out at Wallsend; and I am further indebted to Mr. Beilby for the loan of the lantern slides and specimens with which I have sought to illustrate that process.

And in concluding may I be permitted to recall here the feelings to which that visit to Wallsend gave rise. There, grouped together on the very spot where ended the old wall—the visible symbol of the power and might of a civilisation long since passed away—were some of the characteristic signs of another civilisation ampler and more beneficent. Before me, stretching down to the river, was the factory where a score of workers, clad in helmets and gauntlets and swathed like so many Knights Templar, travel-stained and war-worn, their visages lit up by the yellow soda flames, and their ears half-deafened with the sound of exploding hydrogen—a veritable inferno—were repeating on a Gargantuan scale the little experiment first made a century ago in the cellars of this building; turning out, day and night, hundredweights of the plastic metal in place of the little pin-heads which then burst upon the astonished and delighted gaze of Davy. Behind me was the magnificent power-house—one of the most magnificent of its kind in the world—furnishing not only the electrical energy which transformed the soda into sodium, but diffusing this energy for a multitude of other purposes over an entire district—a noble temple to the genius and prescience of Faraday. Surely one might here say, if you desire to see the monuments of these men, look around! And to my right, and close at hand, was the huge building slip just vacated by the *Mauretania*, herself a symbol of the supremacy of an empire, far mightier, more world-wide, and more potent for good than that which massed its legions behind the old wall.

[T. E. T.]



Friday, January 31, 1908.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. M.A. D.C.L.  
LL.D. Sc.D. Pres.R.S., in the Chair.

PROFESSOR ERNEST RUTHERFORD, M.A. LL.D. D.Sc. F.R.S.

*Recent Researches in Radio-activity.*

IN 1904 I had the honour of giving an address at the Royal Institution on the subject of Radio-activity. In the interval steady and rapid progress has been made in unravelling the tangled skein of radio-active phenomena. In the present lecture I shall endeavour to review very shortly some of the more important advances made in the last few years, but as I cannot hope to mention, even briefly, the whole additions to our knowledge in the various branches of the subject, I shall confine my attention to a few of the more salient facts in the development of which I have taken some small share.

In my previous lecture I based the explanation of radio-active phenomena on the disintegration theory put forward in 1903 by Rutherford and Soddy, which supposes that the atoms of the radio-active bodies are unstable systems which break up with explosive violence. This theory has stood the test of time, and has been invaluable in guiding the experimenter through the maze of radio-active complications. In its simplest form, the theory supposes that every second a certain fraction (usually very small) of the atoms present become unstable and explode with great violence, expelling in many cases a small portion of the disrupted atom at a high speed. The residue of the atom forms a new atomic system of less atomic weight, and possessing physical and chemical properties which markedly distinguish it from the parent atom. The atoms composing the new substance formed by the disintegration of the parent matter are also unstable, and break up in turn. The process of degradation of the atom, once started, proceeds through a number of distinct stages. These new products formed by the successive disintegrations of the parent matter are in most cases present in such extremely minute quantity that they cannot be investigated by ordinary chemical methods. The radiations from these substances, however, afford a very delicate method of qualitative and quantitative analysis, so that we can obtain some idea of the physical and chemical properties of substances existing in an amount which is far below the limit of detection of the balance or spectroscope.

The law that governs the breaking up of atoms is very simple and universal in its application. For any simple substance, the average number of atoms breaking up per second is proportional at any time to the number present. In consequence, the amount of radio-active matter decreases in a geometrical progression with the time. The "period" of any radio-active product, i.e. the time for half the matter to be transformed, is a definite and characteristic property of the product which is uninfluenced by any of the laboratory agents at our command. In fact, the period of any radio-active product, for example, the radium emanation, if determined with sufficient accuracy, might well be taken as a definite standard of time, independent of all terrestrial influences.

The law of radio-active transformation can be very simply and aptly illustrated by an hydraulic analogy. Suppose we take a vertical cylinder filled with water, with an opening near the base through which the water escapes through a high resistance.\* When the discharge is started, the amount of water escaping per second is proportional to the height of water above the zero level of the cylinder. The height of water decreases in a geometrical progression with the time in exactly the same way as the amount of radio-active matter decreases. We can consequently take the height of the column of water as representing the amount of radio-active matter A present at any time. The quantity of water escaping per second is a measure of the rate of disintegration of A and also of the amount of the new substance B formed per second by the disintegration of A. The "period" of the substance is controlled by the amount of resistance in the discharge circuit. A high resistance gives a small flow of water and a long period of transformation, and *vice versa*. By a suitable arrangement we can readily trace out the decay curve for such a case. A cork carrying a light vertical glass rod is floated on the water in the cylinder. A light camel's hair brush is attached at right angles, and moves over the surface of a smoked-glass plate. A vertical line drawn on the glass through the point of contact of the brush gives the axis of ordinates, while a horizontal line drawn through the brush when the water has reached its lowest level gives the axis of abscissæ. If the glass plate is moved with uniform velocity from the moment of starting the discharge, a curve is traced on the glass which is identical in shape with the curve of decay of a radio-active product, where the ordinates at any time represent the relative amount of active matter present, and the abscissæ time. With such an apparatus we can illustrate in a simple way the increase with time of radio-active matter B, which is supplied by the transformation of a substance A. This will correspond, for example, to the growth of the radium emanation with time in a quantity of radium initially freed from emanation. Let us for convenience

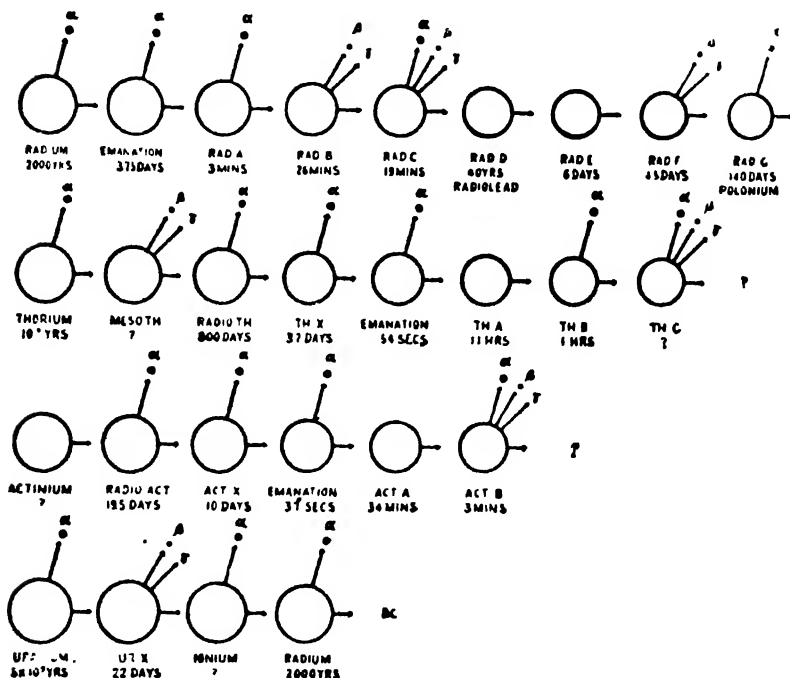
\* A short glass tube in which is placed a plug of glass wool is very suitable.

suppose that A has a much longer period than B. In the hydraulic analogy A is represented by a high head of water discharging at its base through a circuit of high resistance into the top of another cylinder representing the matter B. The water from the cylinder B escapes at its base through a lower resistance. Suppose that initially only A is present. In this case the water in the cylinder B stands at a zero level. On opening the stop-cock connecting with A, water flows into B. The rise of water with time in the cylinder B is traced out in the same way as before by moving the glass plate at a constant rate across the tracing brush. If the period of A is very long compared with that of B the water is supplied to B at a constant rate, and the water in B reaches a constant maximum height when the rate of supply to B equals the rate of escape from the latter. The curve traced out in that case is identical in shape with the "recovery curve" of a radio-active product supplied at a nearly constant rate. The quantity of matter reaches a maximum when the rate of supply equals its own rate of transformation. The relative height of the columns of water in A and B represents at any time the relative amounts of these substances present.

If the period is comparable with that of B, the height of water in B after reaching a maximum falls again, since as the height of A diminishes, the supply to B decreases. Ultimately, the height of B will decrease in a geometrical progression with the time at a rate corresponding to the longer period of the two. This is an exact illustration of the way the amount of a radio-active substance B varies when initially only the parent substance A is present. By using a number of cylinders in series, each with a suitable resistance, we can in a similar way illustrate in a quantitative manner the variation in amount with time of a number of products arising from successive disintegrations of a primary substance. By suitably adjusting the amount of resistance in the discharge circuits of the various cylinders, the curves could be drawn to scale to imitate approximately the variation in amount of the various products with time when the initial conditions are given.

During the last few years a very large amount of work has been done in tracing the remarkable succession of transformations that occur in the various radio-active substances. The known products of radium, thorium, actinium, and uranium are shown graphically below, together with the periods of the products and the character of the radiations they emit. It will be seen that a large list of these unstable bodies are now known. It is probable, however, that not many more remain to be discovered. The main uncertainty lies in the possibility of overlooking a product of rapid transformation following or succeeding one with a very slow period. In tracing out the succession of changes, the emanations or radio-active gases continuously evolved by radium, thorium, and actinium have marked a very definite and important stage, for these emanations can be easily

removed from the radio-active body and their further transformations studied quite apart from the parent element. The analysis of the transformation of the radium emanation has yielded results of great importance and interest. After passing through three stages, radium A, B, and C, of short period, a substance, radium D, of long period, makes its appearance. This is transformed through two stages E and F of short period into radium G, of period 140 days. Meyer and Schweidler have conclusively shown that radium D is the primary constituent of the radio-active substance separated by Hofmann, and called by him radio-lead. Radium G is identical with the first radio-



active substance separated from pitch-blende by Madame Curie, viz. polonium. We are thus sure that these bodies are transformation products of radium. It will be seen that I have added another product of period 4.5 days between radium D and polonium. The presence of such a product has been shown by Meyer and Schweidler.

In the case of thorium, a very long list of products is now known. For several years thorium X was thought to be the first product of thorium, but Hahn has recently shown that at least two other products of slow transformation intervene, which he has called mesothorium and radiothorium. The radiothorium emits  $\alpha$  rays, and

has a period of more than 800 days. Mesothorium apparently emits  $\beta$  rays, and has a still longer period of transformation, the exact value of which has not yet been accurately determined. Since thorium is used commercially on a large scale, there is every prospect that we shall soon be able to obtain considerable quantities of very active preparations of mesothorium and radiothorium. The separation of these bodies from thorium does not in any way alter its commercial value. It is to be hoped that if these active preparations are separated in quantity, the physicist and chemist may be able to obtain a supply of very active material at a reasonable cost, and that there will not be an attempt to compete with the ridiculously high prices charged for radium.

From the radio-active point of view, the radio-elements are only distinguished from their families of products by their comparatively long period of transformation. Now we have reason to believe that radium itself is transformed according to the laws of other radio-active products with a period of about 2000 years. If this be the case, in order to keep up its supply in a mineral, radium must be produced from another substance of relatively long period of transformation. The search for this elusive parent of radium has been one of almost dramatic interest, and illustrates the great importance of the theory as a guide to the experimenter. The view that radium was a substance in continuous transformation was put forward by Rutherford and Soddy in 1903. The most probable parent of radium appeared to be uranium, which has a period of transformation of the order of 1000 million years. If this were the case, uranium, initially freed from radium, should in the course of time grow radium, i.e. radium should again appear in the uranium. This has been tested independently by Soddy and Boltwood, and both have shown that in carefully prepared uranium solutions there is no appreciable growth of radium in the course of several years. The rate of production of radium, if it occurs at all, is certainly less than  $\frac{1}{1000}$  of the amount to be expected from theory. This would appear at first sight to put out of count the view that uranium is the parent of radium. This, however, is by no means the case, for such a result could be very easily explained if one or more substances of very slow period of transformation appeared between uranium and radium. It is obvious that the necessity of forming such an intermediate product would greatly lengthen the time required before an appreciable amount of radium appeared.

There is, however, another indirect but very simple method of attack to settle the parentage of radium. If radium is derived from the transformation of uranium, however many unknown products intervene, the ratio between the amount of radium and uranium in old minerals should be a definite constant. This is obviously the case, provided sufficient time has elapsed for the amount of radium to have reached its equilibrium value. The constancy of this relation

has been completely substantiated by the independent work of Boltwood, Strutt, and McCoy. It has been shown that the quantity of uranium corresponding to 1 gram of radium is  $3.8 \times 10^{-7}$  gram, and is the same for minerals obtained from all parts of the world. Since the radium is always distributed throughout the mass of uranium, we cannot expect to find nuggets of radium like nuggets of gold, unless by some chance the radium has been dissolved out of radio-active minerals and redeposited within the last few thousands of years. To those who had faith in the disintegration theory, this unique constant relation between the amounts of two elements was a satisfactory proof that radium stood in a genetic relation with uranium. A search was then made for the unknown intervening product which, if isolated, must grow radium at a rapid rate. A year or so ago Boltwood observed that a preparation of actinium separated from a uranium mineral did grow radium at a constant but rapid rate. It thus appeared as if actinium were the long-looked-for parent of radium, and that actinium and its long family of products intervened between uranium X and radium. I was, however, able to show that actinium itself was not responsible for the growth of radium, but another unknown substance separated with it. These results were confirmed by Boltwood, who finally succeeded in isolating a new substance from uranium minerals, which was slowly transformed into radium. This substance, which he termed "ionium," has apparently chemical properties similar to those of thorium, and emits  $\alpha$  rays of penetrating power less than those of uranium.

The main previsions of the theory have thus been experimentally verified. Radium is a changing substance the amount of which is kept up by the disintegration of another element, ionium. In order to complete the chain of evidence, we require to show that uranium grows ionium, and it is probable that evidence in this direction will soon be forthcoming. We thus see that we are able to link uranium, ionium, radium, and its long line of descendants, into one family, with uranium as its first parent. As uranium has a period of transformation of more than one thousand million years, it will not be profitable at the moment to try and trace back the family further.

It appears almost certain that, from the radio-active point of view, uranium and thorium must be considered as two independent elements. The case of actinium is different, for Boltwood has shown that the amount of actinium in minerals, like the amount of radium, is proportional to the amount of uranium. This indicates that actinium stands in a genetic relation with uranium. Unless our experimental evidence is at fault, it does not appear probable that actinium belongs to the main line of descent of uranium, for the activity of actinium separated from a mineral compared with radium is only about one-quarter of what we should expect under such conditions. I think that a suggestion which I put forward some time ago may account for the obvious connection of actinium with

uranium, and at the same time for the anomaly observed. This supposes that actinium is a branch descent from some member of the uranium family. It does not appear improbable that at one stage of the disintegration two distinct substances may be produced, one in greater quantity than the other. After the expulsion of an  $\alpha$  particle, it may happen that there are two possible arrangements of temporary stability of the residual atom. The great majority of the atoms may fall into one arrangement, and the remainder into the other. Actinium in this case would correspond to the substance in lesser quantity. It would act as a distinct element, and would break up in a different way from the main amount. It is probable that a large amount of accurate work will be required before the position of actinium in the scheme of changes can be fixed with certainty. It is a matter of remark how closely actinium resembles thorium in its series of transformations. It would appear that the atom of actinium has many points in common with thorium, or rather with its product, mesothorium.

The recent observations on the growth of radium offer a very simple and straightforward method of determining experimentally the period of radium. Suppose that we take a uranium mineral and determine by the emanation method the quantity of radium contained in it. If the immediate parent of radium (i.e. ionium) is next completely separated from the uranium and radium, it will begin to grow radium at a constant rate. Now the rate of growth of radium observed is a measure of the rate of breaking up of the radium parent in the mineral, since before separation the rate of production was equal to the rate of breaking up. Now the growth of radium observed for a short interval, for example, a year, divided by the quantity present in the mineral, gives the fraction of the radium breaking up per year. Proceeding in this way, Boltwood found that the fraction breaking up per year is about  $\frac{1}{2000}$ , and that the period of radium is about 2000 years—a value which lies between the most probable values deduced from quite distinct data.

From an inspection of the radio-active families, it will be seen that out of twenty-six radio-active substances that have been identified, seventeen give out  $\alpha$  rays or  $\alpha$  and  $\beta$  rays, four give out only  $\beta$  rays, and five emit no rays at all. The rayless and  $\beta$ -ray products are transformed according to the same law as the  $\alpha$ -ray products, and there is the same sudden change of physical and chemical properties as the result of the transformation. In the case of the substances which throw off atoms of matter in the form of  $\alpha$  particles, there are obvious reasons for anticipating a change in properties of the substance, but this is not the case for the ray-less or  $\beta$ -ray products. We must either suppose that the mass of the atom is not appreciably changed by the transformation, which consists in an internal rearrangement of the parts of the atom, or that the atom expels a particle at too low a velocity to be appreciated by the

electrical methods. Unfortunately, it is very difficult to study the rayless products with care, as in practically every case they are succeeded by a ray product of comparatively rapid transformation. The rayless products are of great interest as indicating the possibility of transformations which can occur without any detectable radiation.

In the course of the analysis of radio-active changes, special methods have been developed for the separation of the various products from each other. It is only in a few cases, however, that we can hope to obtain a sufficient quantity of the substance to examine by means of the balance. It should be possible to obtain workable quantities of actinium, radium D (radio-lead), and radium G (polonium), but the isolation of these substances in any quantity has not yet been effected. Sir William Ramsay and Mr. Cameron have made a number of important investigations of the properties and volume of the radium emanation, freed so far as possible from any traces of known gases. The remarkable initial contraction of the volume due to the emanation shows that there is still much to be done to obtain a clear understanding of the behaviour of this intensely radio-active gas when obtained in a pure state.

Simultaneously with the work on the analysis of radio-active changes, a large number of investigations have been made on the laws of absorption by matter of the three primary types of radiation from active matter, viz. the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays, and the secondary radiations to which they give rise. It has generally been accepted for some years that the  $\gamma$  rays are a type of penetrating X-rays. The latter are supposed to consist of electro-magnetic pulses in the ether, set up by the impact or escape of electrons from matter, and akin in many respects to very short waves of ultra-violet light. Recently, however, Bragg has challenged this view, and has suggested that the  $\gamma$  rays (and probably also the X-rays) are mainly corpuscular in character, and consist of uncharged particles, or "neutral pairs," as he terms them, projected at a high velocity. Such a view serves to explain most of the experimental observations equally well as the pulse theory; Bragg has recently brought forward additional evidence, based on the direction of the secondary radiation from the  $\gamma$  rays, which he considers to be inexplicable by the pulse theory. We must await further data before this important question can be settled definitely, but the theory of Bragg, which carries many important consequences in its train, certainly deserves very careful examination.

From the radio-active point of view, the  $\alpha$  rays are by far the most important type of radiation emitted by active matter, although their power of penetration is insignificant compared with the  $\beta$  or  $\gamma$  rays. They consist of veritable atoms of matter projected at a speed, on an average, of 6000 miles per second. It is the great energy of motion of these swiftly expelled masses that gives rise to the heating effect of radium. In addition, they are responsible for the greater part of the ionisation observed near an uncovered radio-active sub-



stance. On account of their importance in radio-active phenomena, I shall devote some little attention to the behaviour of these rays. The work of Bragg and Kleeman, of Adelaide, first gave us a clear idea of the nature of the absorption of these rays by matter. The  $\alpha$  particles from a very thin film of any simple kind of radio-active matter are all projected at an identical speed, and lose their power of ionising the gas or of producing phosphorescence or photographic action after they have traversed exactly the same distance, which may conveniently be called the "range" of the  $\alpha$  particle. Now every product emits  $\alpha$  particles at an identical speed among themselves, but different from every other product. For example, the swiftest  $\alpha$  particles from the radium family, viz. that from radium C, travels 7 cm. in air under ordinary conditions before it is stopped, while that from radium itself is projected at a slower speed, travelling only 3.5 cm. We may regard the  $\alpha$  particle as a projectile travelling so swiftly that it plunges through every molecule in its path, producing positively and negatively charged ions in the process. On an average, an  $\alpha$  particle before its career of violence is stopped breaks up about 100,000 molecules. So great is the kinetic energy of the  $\alpha$  projectile that its collisions with matter do not sensibly deflect it, and in this respect it differs markedly from the  $\beta$  particle, which is apparently easily deflected by its passage through matter. At the same time, there is undoubted evidence that the direction of motion of some of the  $\alpha$  particles is slightly changed by their passage through matter.

The sudden cessation of the ionising power produced by the  $\alpha$  particle after traversing a definite distance of air has been shown by Bragg to be a powerful method of analysis of the number of  $\alpha$ -ray products present in a substance. For example, suppose the amount of ionisation in the gas produced by a narrow pencil of  $\alpha$  rays is examined at varying distances from the radium. At a distance of 7 cm. there is a sudden increase in the amount of ionisation, for at this distance the  $\alpha$  particles from radium C enter the testing vessel. There are again sudden changes in the ionisation at distances of 4.8 cm., 4.3 cm., and 3.5 cm. These are due to the rays from the radium A, the emanation and radium itself respectively entering the testing vessel. The  $\alpha$ -ray analysis thus discloses four types of  $\alpha$  rays present in radium in equilibrium—a result in conformity with the more direct analysis. This method allows us to settle at once whether more than one  $\alpha$ -ray product is present in a given radio-active material. For example, an analysis by Hahn by this method of the radiation from the active deposit of thorium has disclosed the existence of two  $\alpha$ -ray products instead of one as previously supposed. We can consequently gain information on the complexity of radio-active material, even though no chemical methods have been found to separate the products concerned. The range of the  $\alpha$  particle from each product is a definite constant which is characteristic of each product.

The  $\alpha$  particle decreases in velocity as it passes through matter. This result is clearly brought out by photographs showing the deflection of a homogeneous pencil of  $\alpha$  rays in a magnetic field before and after passing through an absorbing screen. The greater divergence of the trace of the  $\alpha$  rays on the plate, after passing through the screen, shows that their velocity is reduced, while the sharpness of the band shows that the  $\alpha$  particles still move at an identical speed.

In order to make an accurate determination of the constants of the  $\alpha$  particles, it is necessary to work with homogeneous rays, and we consequently require to use a thin layer of matter of one kind. For experiments of this character, a wire coated with a thin film of radium C by exposure to the radium emanation is very suitable. The velocity of the  $\alpha$  particle and the value  $e/m$ , the ratio of the charge carried by the  $\alpha$  particle to its mass, can be deduced by observing the deflections of a pencil of  $\alpha$  rays exposed in a magnetic and in an electric field of known strengths. The deflection of a pencil of  $\alpha$  rays in an electric field is small under normal conditions, and special care is needed to determine it with accuracy.

In this way I have calculated the velocity and value of  $e/m$  for a number of  $\alpha$ -ray products. The velocity of expulsion varies for different products, but is connected by a simple relation with the range of the  $\alpha$  particle in air. The value of  $e/m$  has been determined for selected products of radium, thorium, and actinium, and in each case the same value has been found. This shows that the  $\alpha$  particles expelled from radio-active substances in general are identical in constitution. They have all the same mass, but differ from one another in the initial velocity of their projection. Although we are sure that the  $\alpha$  particles, from whatever source, are identical atoms of matter, we are still unable to settle definitely the true nature of the  $\alpha$  particle. The value of  $e/m$  found by experiment is nearly  $5 \times 10^3$ . Now the value of  $e/m$  for the hydrogen atom in the electrolysis of water is  $10^4$ . If the charge carried by the  $\alpha$  particle and the hydrogen atom is the same, the mass of the  $\alpha$  particle is twice that of the hydrogen atom, i.e. a mass equal to the hydrogen molecule. But we are not certain that they do carry the same charge. Here we are, unfortunately, confronted by a number of possibilities, for the magnitude of  $m$  for the  $\alpha$  particle is conditioned by the value assumed for  $e$ . If the charge of the  $\alpha$  particle is assumed to be twice the value of the hydrogen atom, the mass comes out four times the hydrogen atom—the value found for the helium atom. The weight of evidence still supports the view that the  $\alpha$  particle is in some way connected with the helium atom. If the  $\alpha$  particle is a helium atom with twice the ionic charge, we must regard the helium produced by radio-active bodies as actually the collected  $\alpha$  particles the charges of which have been neutralised. This at once offers a reasonable explanation of the production of helium by actinium as well as by radium. In addition, Strutt has recently contributed strong evidence that helium is a

product of thorium. Such results are only to be expected on the above view, since the  $\alpha$  particle is the only common product of these elements.

The determination of the true character of the  $\alpha$  particle is one of the most pressing unsolved problems in radio-activity, for a number of important consequences follow from its solution. Unfortunately, a direct experimental proof of its true character appears to be very difficult unless a new method of attack is found. We have seen that if the charge carried by the  $\alpha$  particle could be experimentally determined, the actual value of  $m$  could be determined in terms of the hydrogen atom, since the value of the charge carried by the latter is known. This could be done if we could devise a method of detecting the emission of a single  $\alpha$  particle, and thus counting the number of particles expelled from a known quantity of a radio-active substance, for example, from radium. In considering a possible method of attack of this question, the remarkable property of the  $\alpha$  particles of producing scintillations in zinc sulphide at once suggests itself. Apart from the difficulty of counting the scintillations, it is very doubtful whether more than a small fraction of the  $\alpha$  particles which strike the screen produce the scintillations. Viewed from the electrical side, a simple calculation from the data at our disposal shows that the ionisation produced in a gas by a single  $\alpha$  particle should be detectable. The electrometer or electroscope used for measurement would, however, require to be extremely sensitive, and under such conditions it is known that small electrical disturbances are very difficult to avoid.

In order to obtain a reasonably large effect, we require some method of magnifying the ionisation produced by the  $\alpha$  particle. In conjunction with Dr. Hans Geiger, I have recently developed a method whereby the electrical effect produced by the  $\alpha$  particle can be magnified several thousand times. From the work of Townsend it is known that if a strong electric field acts on gas at low pressure, any ions generated in the gas by an external agency are set in motion by the electric field, and under the proper conditions produce fresh ions by collision with the gas molecules. The negative ion is the most effective ioniser in weak fields, but when the voltage is increased near the point at which a discharge passes, the positive ion also produces fresh ions by collision. In the experimental arrangement the  $\alpha$  particle from the active matter is fired through a small opening about 2 mm. in diameter, covered with a thin layer of mica, into a cylinder 60 cm. long and 2.5 cm. in diameter, in which the gas pressure is about 3 cm. of mercury. A thin insulated wire connected to the electrometer is fixed centrally in the cylinder. If the outside cylinder is charged negatively, for a difference of potential of about 1000 volts any ionisation produced in the cylinder is increased about 2000 times by collision. This can be simply illustrated by using the  $\gamma$  rays of radium as a source of ionisation. When a difference of potential is applied to the cylinder, the ionisation produced by the  $\gamma$

rays only causes a slight movement of the electrometer needle. By applying, however, a voltage nearly equal to that required for a discharge through the gas there is a very rapid movement of the needle. On removing the radium there is no appreciable current through the gas. On placing a source of  $\alpha$  rays near the small opening in the cylinder so that some of the  $\alpha$  particles can be fired along the axis of the cylinder, the electrometer needle does not move uniformly, but with a succession of rapid throws with a considerable interval in between. Each of these throws is due to the discharge produced by a single  $\alpha$  particle entering the cylinder, increased several thousand times by the intermediary of the strong electric field. If a sheet of paper which stops the  $\alpha$  rays is placed before the opening, the electrometer needle at once comes to rest. The interval of time between the throws is not uniform. This is exactly what we should expect if the number of  $\alpha$  particles entering such a small opening is governed by the law of probability. On the average, a certain number of  $\alpha$  particles are fired through the opening per minute, but in some cases the interval is less than the average, in others much greater. In fact, by observing the intervals between the entrance of a large number of  $\alpha$  particles, we should be able to determine accurately the "probability" curve of distribution of the  $\alpha$  particles with time. For purposes of measurements, the active material, in the form of a thin film covering a small area, is placed in an exhausted tube connected in series with the ionisation cylinder, and at a considerable distance from the hole. The number of  $\alpha$  particles entering the opening per minute is counted, and from this the total number expelled can be calculated. Preliminary measurements show that the number of  $\alpha$  particles expelled from a known weight of radium is of the same order as the calculated value. When the measurements are completed it should be possible to determine the charge carried by each  $\alpha$  particle, since the total charge carried by the  $\alpha$  particles from 1 gram of radium is known. In this way it may be possible to settle whether the  $\alpha$  particle is a helium atom or not. In any case, it is a matter of some interest to be able to detect by its electrical effect a single atom of matter, and so to determine directly with a minimum of assumption the magnitude of some of the most important quantities in radioactive phenomena.

[E. R.]

Friday, February 21, 1908.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. M.A. D.C.L. LL.D.  
Sc.D. Pres.R.S., in the Chair.

SIR OLIVER LODGE, LL.D. D.Sc. F.R.S. *M.R.I.*

*The Ether of Space.*

[ABSTRACT.]

THIRTY years ago Clerk Maxwell gave in this place a remarkable address on "Action at a Distance." It is reported in your Journal, Vol. VII., and to it I would direct attention. Most natural philosophers hold, and have held, that action at a distance across empty space is impossible; in other words, that matter cannot act where it is not, but only where it is. The question "where is it?" is a further question that may demand attention and require more than a superficial answer. For it can be argued on the hydrodynamic or vortex theory of matter, as well as on the electrical theory, that every atom of matter has a universal though nearly infinitesimal prevalence, and extends everywhere; since there is no definite sharp boundary or limiting periphery to the region disturbed by its existence. The lines of force of an isolated electric charge extend throughout illimitable space. And though a charge of opposite sign will curve and concentrate them, yet it is possible to deal with both charges, by the method of superposition, as if they each existed separately without the other. In that case, therefore, however far they reach, such nuclei clearly exert no "action at a distance" in the technical sense.

Some philosophers have reason to suppose that mind can act directly on mind without intervening mechanism, and sometimes that has been spoken of as genuine action at a distance; but, in the first place, no proper conception or physical model can be made of such a process, nor is it clear that space and distance have any particular meaning in the region of psychology. The links between mind and mind may be something quite other than physical proximity, and in denying action at a distance across empty space I am not denying telepathy or other activities of a non-physical kind; for although brain disturbance is certainly physical and is an essential

concomitant of mental action, whether of the sending or receiving variety, yet we know from the case of heat that a material movement can be excited in one place at the expense of corresponding movement in another, without any similar kind of transmission or material connection between the two places: the thing that travels across vacuum is not heat.

In all cases where physical motion is involved, however, I would have a medium sought for; it may not be matter, but it must be something; there must be a connecting link of some kind, or the transference cannot occur. There can be no attraction across really empty space. And even when a material link exists, so that the connexion is obvious, the explanation is not complete; for when the mechanism of attraction is understood, it will be found that a body really only moves because it is pushed by something from behind. The essential force in nature is the *vis à tergo*. So when we have found the "traces," or discovered the connecting thread, we still run up against the word "cohesion," and ought to be exercised in our minds as to its ultimate meaning. Why the whole of a rod should follow, when one end is pulled, is a matter requiring explanation; and the only explanation that can be given involves, in some form or other, a continuous medium connecting the discrete and separated particles or atoms of matter.

When a steel spring is bent or distorted, what is it that is really strained? Not the atoms—the atoms are only displaced; it is the connecting links that are strained—the connecting medium—the ether. Distortion of a spring is really distortion of the ether. All stress exists in the ether. Matter can only be moved. Contact does not exist between the atoms of matter as we know them; it is doubtful if a piece of matter ever touches another piece, any more than a comet touches the sun when it appears to rebound from it; but the atoms are connected, as the comet and the sun are connected, by a continuous *plenum* without break or discontinuity of any kind. Matter acts on matter only through the ether. But whether matter is a thing utterly distinct and separate from the ether, or whether it is a specifically modified portion of it—modified in such a way as to be susceptible of locomotion, and yet continuous with all the rest of the ether, which can be said to extend everywhere—far beyond the bounds of the modified and tangible portion—are questions demanding, and I may say in process of receiving, answers.

Every such answer involves some view of the universal and possibly infinite uniform omnipresent connecting medium, the Ether of space.

It has been said, somewhat sarcastically, that the ether was made in England. The statement is only an exaggeration of the truth. I might even urge that it has been largely constructed in the Royal Institution; for, I will remind you now of the chief lines of evidence on which its existence is believed in, and our knowledge of it is

based. First of all, Newton recognised the need of a medium for explaining gravitation. In his "Optical Queries" he shows that if the pressure of this medium is less in the neighbourhood of dense bodies than at great distances from them, dense bodies will be driven towards each other; and that if the diminution of pressure is inversely as the distance from the dense body, the law will be that of gravitation.

All that is required, therefore, to explain gravity is a diminution of pressure, or increase of tension, caused by the formation of a matter unit—that is to say of an electron or corpuscle; and although we do not yet know what an electron is—whether it be a strain centre, or what kind of singularity in the ether it may be—there is no difficulty in supposing that a slight, almost infinitesimal, strain or attempted rarefaction should be produced in the ether whenever an electron came into being—to be relaxed again only on its resolution and destruction. Strictly speaking it is not a real *strain*, but only a "stress"; since there can be no actual *yield*, but only a pull or tension, extending in all directions towards infinity.

The tension required per unit of matter is almost ludicrously small, and yet in the aggregate, near such a body as a planet, it becomes enormous.

The force with which the moon is held in its orbit would be great enough to tear asunder a steel rod four hundred miles thick, with a tenacity of 30 tons per square inch; so that if the moon and earth were connected by steel instead of by gravity, a forest of pillars would be necessary to whirl the system once a month round their common centre of gravity. Such a force necessarily implies enormous tension or pressure in the medium. Maxwell calculates that the gravitational stress near the earth, which we must suppose to exist in the invisible medium, is 3000 times greater than what the strongest steel could stand; and near the sun it should be 2500 times as great as that.

The question has arisen in my mind, whether, if the whole sensible universe—estimated by Lord Kelvin as equivalent to about a thousand million suns—were all concentrated in one body of specifiable density,\* the stress would not be so great as to produce a tendency towards etherial disruption: which would result in a disintegrating explosion, and a scattering of the particles once more as an enormous nebula and other fragments into the depths of space. For the tension would be a maximum in the interior of such a mass; and, if it rose to the value  $10^{83}$  dynes per square centimetre, something would have to happen. I do not suppose that this can be the reason, but one would think there must be *some* reason, for the scattered condition of gravitative matter.

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\* On doing the arithmetic, however, I find the necessary concentration absurdly great, showing that such a mass is quite insufficient. See Appendix.

Too little is known, however, about the mechanism of gravitation to enable us to adduce it as the strongest argument in support of the existence of an ether. The oldest valid and conclusive requisition of an ethereal medium depends on the wave theory of light, one of the founders of which was your Professor of Natural Philosophy at the beginning of last century, Dr. Thomas Young.

No ordinary matter is capable of transmitting the undulations or tremors that we call light. The speed at which they go, the kind of undulation, and the facility with which they go through vacuum, forbid this.

So clearly and universally has it been perceived that waves must be waves of something—something distinct from ordinary matter—that Lord Salisbury, in his presidential address to the British Association at Oxford, criticised the ether as little more than a nominative case to the verb to undulate. It is truly *that*, though it is also truly more than that; but to illustrate that luminiferous aspect of it, I will quote a paragraph from that lecture of Clerk Maxwell's to which I have already referred:—

“The vast interplanetary and interstellar regions will no longer be regarded as waste places in the universe, which the Creator has not seen fit to fill with the symbols of the manifold order of His kingdom. We shall find them to be already full of this wonderful medium; so full, that no human power can remove it from the smallest portion of space, or produce the slightest flaw in its infinite continuity. It extends unbroken from star to star; and when a molecule of hydrogen vibrates in the dog-star, the medium receives the impulses of these vibrations, and after carrying them in its immense bosom for several years, delivers them, in due course, regular order, and full tale, into the spectroscope of Mr. Huggins, at Tulse Hill.” (It is pleasant to remember that those veteran investigators Sir William and Lady Huggins are still at work.)

This will suffice to emphasise the fact that the eye is truly an ethereal sense-organ—the only one which we possess, the only mode by which the ether is enabled to appeal to us, and that the detection of tremors in this medium—the perception of the direction in which they go, and some inference as to the quality of the object which has emitted them—cover all that we mean by “sight” and “seeing.”

I pass then to another function, the electric and magnetic phenomena displayed by the ether; and on this I will only permit myself a very short quotation from the writings of Faraday, whose whole life may be said to have been directed towards a better understanding of these ethereal phenomena. Indeed, the statue in your entrance hall may be considered as the statue of the discoverer of the electric and magnetic properties of the Ether of space.

Faraday conjectured that the same medium which is concerned in the propagation of light might also be the agent in electromagnetic phenomena. “For my own part,” he says, “considering the relation



of a vacuum to the magnetic force, and the general character of magnetic phenomena external to the magnet, I am much more inclined to the notion that in the transmission of the force there is such an action, external to the magnet, than that the effects are merely attraction and repulsion at a distance. Such an action may be a function of the æther; for it is not unlikely that, if there be an æther, it should have other uses than simply the conveyance of radiation."

This conjecture has been amply strengthened by subsequent investigations.

One more function is now being discovered; the ether is being found to constitute matter—an immensely interesting topic, on which there are many active workers at the present time. I will make a brief quotation from your present Professor of Natural Philosophy (J. J. Thomson), where he summarises the conclusion which we all see looming before us, though it has not yet been completely attained, and would not by all be similarly expressed:—

"The *whole* mass of any body is just the mass of ether surrounding the body which is carried along by the Faraday tubes associated with the atoms of the body. In fact, all mass is mass of the ether; all momentum, momentum of the ether; and all kinetic energy, kinetic energy of the ether. This view, it should be said, requires the density of the ether to be immensely greater than that of any known substance."

Yes, far denser—so dense that matter by comparison is like gossamer, or a filmy imperceptible mist, or a milky way. Not unreal or unimportant—a cobweb is not unreal, nor to certain creatures is it unimportant, but it cannot be said to be massive or dense; and matter, even platinum, is not dense when compared with the ether. Not till last year, however, did I realise what the density of the ether must really be,\* compared with that modification of it which appeals to our senses as matter, and which for that reason engrosses our attention. If I have time I will return to that before I have finished.

Is there any other function possessed by the ether, which, though not yet discovered, may lie within the bounds of possibility for future discovery? I believe there is, but it is too speculative to refer to, beyond saying that it has been urged as probable by the authors of "The Unseen Universe," and has been thus tentatively referred to by Clerk Maxwell:—

"Whether this vast homogeneous expanse of isotropic matter is fitted not only to be a medium of physical interaction between distant bodies, and to fulfil other physical functions of which, perhaps, we have as yet no conception, but also . . . to constitute the material organism of beings exercising functions of life and mind as high or

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\* See Lodge, *Phil. Mag.*, April 1907.

higher than ours are at present—is a question far transcending the limits of physical speculation.”

And there for the present I leave that aspect of the subject.

I shall now attempt to illustrate some relations between ether and matter.

The question is often asked, is ether material? This is largely a question of words and convenience. Undoubtedly, the ether belongs to the material or physical universe, but it is not ordinary matter. I should prefer to say it is not “matter” at all. It may be the substance or substratum or material of which matter is composed, but it would be confusing and inconvenient not to be able to discriminate between matter on the one hand, and ether on the other. If you tie a knot on a bit of string, the knot is composed of string, but the string is not composed of knots. If you have a smoke or vortex-ring in the air, the vortex-ring is made of air, but the atmosphere is not a vortex-ring; and it would be only confusing to say that it was.

The essential distinction between matter and ether is that matter *moves*, in the sense that it has the property of locomotion and can effect impact and bombardment: while ether is *strained*, and has the property of exerting stress and recoil. All potential energy exists in the ether. It may vibrate, and it may rotate, but as regards locomotion it is stationary—the most stationary body we know—absolutely stationary, so to speak; our standard of rest.

All that we ourselves can effect, in the material universe, is to alter the motion and configuration of masses of matter; we can move matter, by our muscles, and that is all we can do directly: everything else is indirect.

But now comes the question, how is it possible for matter to be composed of ether? How is it possible for a solid to be made out of fluid? A solid possesses the properties of rigidity, impenetrability, elasticity, and such like; how can these be imitated by a perfect fluid such as the ether must be? The answer is, they can be imitated by a fluid in motion; a statement which we make with confidence as the result of a great part of Lord Kelvin's work.

It may be illustrated by a few experiments.

A wheel of spokes, transparent or permeable when stationary, becomes opaque when revolving, so that a ball thrown against it does not go through, but rebounds. The motion only affects permeability to matter; transparency to light is unaffected.

A silk cord hanging from a pulley becomes rigid and viscous when put into rapid motion; and pulses or waves which may be generated on the cord travel along it with a speed equal to its own velocity, whatever that velocity may be, so that they appear to stand still. This is a case of kinetic rigidity; and the fact that the wave-transmission velocity is equal to the rotatory speed of the material, is typical and

important, for in all cases of kinetic elasticity these two velocities are of the same order of magnitude.

A flexible chain, set spinning, can stand up on end while the motion continues.

A jet of water at sufficient speed can be struck with a hammer, and resists being cut with a sword.

A spinning disk of paper becomes elastic like flexible metal, and can act like a circular saw. Sir William White tells me that in naval construction steel plates are cut by a rapidly revolving disk of soft iron.

A vortex-ring, ejected from an elliptical orifice, oscillates about the stable circular form, as an indiarubber ring would do; thus furnishing a beautiful example of kinetic elasticity, and showing us clearly a fluid displaying some of the properties of a solid.

A still further example is Lord Kelvin's model of a spring balance, made of nothing but rigid bodies in spinning motion.\*

If the ether can be set spinning, therefore, we may have some hope of making it imitate the properties of matter, or even of constructing matter by its aid. But how are we to spin the ether? Matter alone seems to have no grip of it. I have spun steel disks, a yard in diameter, 4000 times a minute, have sent light round and round between them, and tested carefully for the slightest effect on the ether. Not the slightest effect was perceptible. We cannot spin ether mechanically.

But we can vibrate it electrically; and every source of radiation does that. An electrified body, in sufficiently rapid vibration, is the only source of ether-waves that we know; and if an electric charge is suddenly stopped, it generates the pulses known as X-rays, as the result of the collision. Not speed, but sudden change of speed, is the necessary condition for generating waves in the ether by electricity.

We can also infer some kind of rotary motion in the ether; though we have no such obvious means of detecting the spin as is furnished by vision for detecting some kinds of vibration. It is supposed to exist whenever we put a charge into the neighbourhood of a magnetic pole. Round the line joining the two, the ether is spinning like a top. I do not say it is spinning fast: that is a question of its density; it is in fact spinning with excessive slowness, but it is spinning with a definite moment of momentum. J. J. Thomson's theory makes its moment of momentum exactly equal to  $em$ , the product of charge and pole; the charge being measured electrostatically and the pole magnetically.

How can this be shown experimentally? Suppose we had a spinning top enclosed in a case, so that the spin was unrecognisable by ordinary means—it could be detected by its gyrostatic behaviour to

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\* Address to Section A of British Association at Montreal, 1884.

force. If allowed to "precess" it will respond by moving perpendicularly to a deflecting force. So it is with the charge and the magnetic pole. Try to move the charge suddenly, and it immediately sets off at right angles. A moving charge is a current, and the pole and the current try to revolve round one another—a true gyrostatic action due to the otherwise unrecognisable etherial spin. The fact of such magnetic rotation was discovered by Faraday.

I know that it is usually worked out in another way, in terms of lines of force and the rest of the circuit; but I am thinking of a current as a stream of projected charges; and no one way of regarding such a matter is likely to exhaust the truth, or to exclude other modes which are equally valid. Anyhow, in whatever way it is regarded, it is an example of the three rectangular vectors.

The three vectors at right angles to each other, which may be labelled Current, Magnetism, and Motion respectively, or more generally E, H, and V, represent the quite fundamental relation between ether and matter, and constitute the link between Electricity, Magnetism, and Mechanics. Where any two of these are present, the third is a necessary consequence. This principle is the basis of all dynamos, of electric motors, of light, of telegraphy, and of most other things. Indeed, it is a question whether it does not underlie everything that we know in the whole of the physical sciences; and whether it is not the basis of our conception of the three dimensions of space.

Lastly, we have the fundamental property of matter called *inertia*, which, if I had time, I would show could be explained electromagnetically, provided the etherial density is granted as of the order  $10^{12}$  grammes per cubic centimetre. The elasticity of the ether would then have to be of the order  $10^{33}$  c.g.s.; and if this is due to intrinsic turbulence, the speed of the whirling or rotational elasticity must be of the same order as the velocity of light. This follows hydrodynamically; in the same sort of way as the speed at which a pulse travels on a flexible running endless cord, whose tension is entirely due to the centrifugal force of the motion, is precisely equal to the velocity of the cord itself. And so, on our present view, the intrinsic energy of constitution of the ether is incredibly and portentously great; every cubic millimetre of space possessing what, if it were matter, would be a mass of a thousand tons, and an energy equivalent to the out-put of a million-horse-power-station for 40 million years.

The universe we are living in is an extraordinary one; and our investigation of it has only just begun. We know that matter has a psychical significance, since it can constitute *brain*, which links together the physical and the psychical worlds. If anyone thinks that the ether, with all its massiveness and energy, has probably no psychical significance, I find myself unable to agree with him.

## APPENDIX I. ON GRAVITY AND ETHERIAL TENSION.

Stating the law of gravitation as  $F = \gamma \frac{m m'}{r^2}$ , the meaning here adopted for etherial tension at the surface of the Earth is

$$T = \int_R^\infty \frac{\gamma E}{r^2} dr = \frac{\gamma E}{R};$$

so that the ordinary intensity of gravity is

$$g = -\frac{dT}{dR} = \frac{\gamma E}{R^2} = \frac{4}{3} \pi \rho \gamma R.$$

Accordingly, near the surface of a planet the tension is  $T_0 = g R$ , or for different planets is proportional to  $\rho R^2$ .

The velocity of free fall from infinity to such a planet is  $\sqrt{2 T_0}$ ; the velocity of free fall from circumference to centre, assuming uniform distribution of density, is  $\sqrt{(T_0)}$ ; and from infinity to centre it is  $\sqrt{(3 T_0)}$ .

Expanding all this into words:—

The etherial tension near the earth's surface, required to explain gravity by its rate of variation, is of the order  $6 \times 10^{11}$  c.g.s. units. The tension near the sun is 2500 times as great. With different spheres in general, it is proportional to the density and to the superficial area. Hence, near a bullet one inch in diameter, it is of the order  $10^{-6}$ ; and near an atom or electron about  $10^{-21}$ .

In order to set up a tension equal to the critical, or presumably disruptive, stress in the ether [ $10^{33}$  c.g.s.], a globe of the density of the earth would have to have a radius of eight light years. In order to generate a velocity of free fall under gravity equal to the velocity of light, a globe of the earth's density would have to be equal in radius to the distance of the earth from the sun, or say 26,000 times the earth's radius. If the density were less, the superficial area would have to be increased in proportion, so as to keep  $\rho R^2$  constant.

The whole visible universe within a parallax of  $\frac{1}{10000}$  second of arc, estimated by Lord Kelvin as the equivalent of  $10^9$  suns, would be quite incompetent to raise etherial tension to the critical point  $10^{33}$  c.g.s. unless it were concentrated to an absurd degree; but it could generate the velocity of light with a density comparable to that of water.

If the average density of the above visible universe (which may be taken as  $1.6 \times 10^{-23}$  grammes per c.c.) continued without limit, a disruptive tension of the ether would be reached when the radius was comparable to  $10^{13}$  light years; and the velocity of light would

be generated by it when the radius was  $10^7$  light years. But heterogeneity would enable these values to be reached *more* easily.

It is noteworthy how exceedingly small is the average or aggregate density of matter in the visible region of space; and Lord Kelvin has shown that throughout space in general it must be smaller still—in fact ultimately infinitesimal.

The estimated density of  $10^{-23}$  c.g.s. means that the visible cosmos is as much rarer than a vacuum of a hundred millionths of an atmosphere, as that vacuum is itself rarer than lead.

It is, of course, because ordinary masses of matter likewise consist of separated particles, with great intervening distances in proportion to their size, that we are able to assert the minute aggregate density of ordinary stuff, such as water or lead, as compared with the continuous medium of which all particles are supposed to be really composed. The fundamental medium itself must be of uniform density everywhere, whether materialised or free.

## APPENDIX II. EXPLANATORY REMARKS CONCERNING THE DENSITY OF ETHER.

I observe that it is surmised by at least one thoughtful and friendly critic—C. W. S. in the *Westminster Gazette*—that in speaking of the immense density or massiveness of ether, and the absurdly small density or specific gravity of gross matter by comparison, I intended to signify that matter is a *rarefaction* of the ether. That, however, was not my intention. The view I advocate is that the ether is a perfect *continuum*, an absolute *plenum*, and that therefore no rarefaction is possible. The ether inside matter is just as dense as the ether outside, and no denser. A material unit—say an electron—is only a peculiarity or singularity of some kind in the ether itself, which is of perfectly uniform density everywhere. What we sense as matter is an aggregate or grouping of an enormous number of such units.

How then can we say that matter is millions of times rarer or less substantial than the ether of which it is essentially composed? Those who feel any difficulty here, should bethink themselves of what they mean by the average or aggregate density of any discontinuous system, such as a powder, or a gas, or a precipitate, or a snowstorm, or a cloud, or a milky way.

If it be urged that it is unfair to compare an obviously discrete assemblage like the stars, with an apparently continuous substance like air or lead, the answer is that it is entirely and accurately fair; since air, and every other known form of matter, is essentially an aggregate of particles, and since it is always their average density that we mean. We do not even know for certain their individual atomic density.

The phrase “specific gravity or density of a powder” is ambigu-

ous. It may mean the specific gravity of the dry powder as it lies, like snow ; or it may mean the specific gravity of the particles of which it is composed, like ice.

So also with regard to the density of matter, we might mean the density of the fundamental material of which its units are made—which would be ether ; or we might, and in practice do, mean the density of the aggregate lump which we can see and handle ; that is to say, of water or iron or lead, as the case may be.

In saying that the density of matter is small, I mean, of course, in the last, the usual, sense. In saying that the density of ether is great, I mean that the actual stuff of which these highly porous aggregates are composed is of immense, of well-nigh incredible, density. It is only another way of saying that the ultimate units of matter are few and far between—i.e. that they are excessively small as compared with the distances between them ; just as the planets of the solar system, or worlds in the sky, are few and far between—the intervening distances being enormous as compared with the portions of space actually occupied by lumps of matter.

Here it may be noted that it is possible to argue that the density of a *continuum* is necessarily greater than the density of any disconnected aggregate : certainly of any assemblage whose particles are actually composed of the material of the *continuum*. Because the former is “all there,” everywhere, without break or intermitence of any kind ; while the latter has gaps in it—it is here, and there, but not everywhere.

Indeed, this very argument was used long ago by that notable genius Robert Hooke, and I quote a passage which Professor Poynting has discovered in his collected posthumous works, and kindly copied out for me :—

“As for *matter*, that I conceive in its essence to be immutable, and its essence being expatiation determinate, it cannot be altered in its quantity, either by condensation or rarefaction ; that is, there cannot be more or less of that power or reality, whatever it be, within the same expatiation or content ; but every equal expatiation contains, is filled, or is an equal quantity of *materia* ; and the densest or heaviest, or most powerful body in the world contains no more *materia* than that which we conceive to be the rarest, thinnest, lightest, or least powerful body of all ; as gold for instance, and *æther*, or the substance that fills the cavity of an exhausted vessel, or cavity of the glass of a barometer above the quicksilver. Nay, as I shall afterwards prove, this cavity is more full, or a more dense body of *æther*, in the common sense or acceptation of the word, than gold is of gold, bulk for bulk ; and that because the one, viz., the mass of *æther*, is all *æther* : but the mass of gold, which we conceive, is not all gold ; but there is an intermixture, and that vastly more than is commonly supposed, of *æther* with it ; so that vacuity, as it is commonly thought, or erroneously supposed, is a more dense body than

the gold as gold. But if we consider the whole content of the one with that of the other, within the same or equal quantity of expatiation, then are they both equally containing the *materia* or body."

[From the *Posthumous Works of Robert Hooke, M.D., F.R.S.*, 1705, pp. 171-2 (as copied in *Memoir of Dalton*, by Angus Smith).]

Newton's contemporaries did not excel in power of clear expression, as he himself did, but Professor Poynting interprets this singular attempt at utterance thus: "All space is filled with equally dense *materia*. Gold fills only a small fraction of the space assigned to it, and yet has a big mass. How much greater must be the total mass filling that space."

The tacit assumption here made is that the particles of the aggregate are all composed of one and the same continuous substance, practically that matter is made of ether; and that assumption, in Hooke's day, must have been only a speculation. But it is the kind of speculation which time is justifying, it is the kind of truth which we all feel to be in process of establishment now.

We do not depend on that sort of argument however; what we depend on is experimental measure of the mass, and mathematical estimate of the volume, of the electron. For calculation shows that however the mass be accounted for, whether electrostatically or magnetically, or hydrodynamically, the estimate of ratio of mass to effective volume can differ only in a numerical coefficient, and cannot differ as regards order of magnitude. The only way out of this conclusion would be the discovery that the negative electron is not the real or the main matter-unit, but is only a subsidiary ingredient, whereas the main mass is the more bulky positive charge. That last hypothesis however is at present too vague to be useful. Moreover, the mass of such a charge would in that case be unexplained, and would need a further step, which would probably land us in much the same sort of ethereal density as is involved in the estimate which I have based on the more familiar and tractable negative electron.

It may be said why assume any finite density for the ether at all? Why not assume that, as it is infinitely continuous, so it is infinitely dense—whatever that may mean—and that all its properties are infinite? This might be possible were it not for the velocity of light. By transmitting waves at a finite and measurable speed, the ether has given itself away, and has let in all the possibilities of calculation and numerical statement. Its properties are thereby exhibited as essentially finite—however infinite the whole extent of it may turn out to be.

[O. T.]



Friday, February 28, 1908.

GEORGE MATTHEY, ESQ., F.R.S., in the Chair.

PROFESSOR WILLIAM ARTHUR BONE, D.Sc. Ph.D. F.R.S.

*Explosive Combustion, with Special Reference to that of  
Hydrocarbons.*

It is hardly necessary to remind you that the subject of my discourse will be ever associated with the illustrious name of Davy. Davy turned his attention to the phenomena of flame in the year 1815, in response to an urgent appeal on the part of a committee formed in the North of England, to investigate the causes of accidents arising from the explosion of fire-damp in coal mines, and to devise means for their prevention. The perennial interest of his researches, however, lies not so much in their immediate practical success, great as this undoubtedly was, as in the broader theoretical issues which were disclosed, and brought within the region of experimental enquiry, by so splendid an exercise of genius.

Davy insisted on the necessity of considering flames in all cases "As the combustion of an *explosive mixture* of inflammable gas, or vapour, and air," and he defined flame as "aëriiform, or gaseous matter, heated to such a degree as to be luminous." For the starting and propagation of a flame in an explosive mixture, he showed that each successive layer of gas must be raised to a certain definite temperature, called the "ignition point," and he investigated both the ignition temperatures and the explosion limits of a large number of the commoner combustible gases. He then proceeded to his famous discovery that, notwithstanding the extremely high temperatures of flames, which, in the case of cyanogen, he estimated to be "above 5000° of Fahrenheit," they can be readily extinguished by contact with a cooling surface of sufficient area and heat-conducting power. and that for this purpose metal surfaces are by far the most efficient. How he developed and applied this discovery to the construction of his "safe-lamp" for miners is, of course, a matter of history.

In experimenting upon the ignition temperatures of explosive mixtures, Davy made the important and far-reaching discovery that combustible gases combine with oxygen at lower temperatures without any appearance of flame whatever. He emphasised the importance of a complete investigation of the chemical aspects of this

flameless combustion, and he himself was led to ask whether, seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be raised to incandescence by the slow combustion of two gases "without actual flame, but producing heat enough to keep the wire ignited." In this way he discovered the remarkable property of platinum and other metallic wires of inducing surface combustion, and in the course of his further experiments on this subject, he made two notable observations respecting the burning of compounds containing carbon and hydrogen. He found "much carbonic oxide" produced when a platinum wire was kept incandescent by the slow combustion of a mixture of ethylene and oxygen, rendered non-explosive by an excess of the hydrocarbon, and in a similar experiment with ether vapour, he recorded the appearance of "a pale phosphorescent light" accompanied by "the formation of a peculiar acrid volatile substance possessed of acid properties."

Finally, in speculating upon the difficult and thorny subject of the luminosity of hydrocarbon flames, he was "led to imagine" that it "might be owing to the *decomposition* of part of the gas towards the interior of the flame where the air was in smallest quantity, and the deposition of solid charcoal, which, first by its *ignition*, and afterwards by its *combustion*, increased in a high degree the intensity of the light." It is important to observe that not only did Davy rightly attribute the luminosity of a hydrocarbon flame to the presence therein of incandescent carbon, but also that he avoided the error of attributing the separation of carbon to a supposed preferential burning of hydrogen.

In considering the propagation of a flame through an explosive mixture of gases, it is necessary to distinguish between two well-defined conditions. When such a mixture is ignited, the flame travels for a certain limited distance (a few feet only) at a fairly uniform slow velocity, which in the case of a mixture of hydrogen and oxygen in their combining ratios is approximately 34 metres (38 yards) per second. This initial stage of the combustion is called "*inflammation*."

After traversing a few feet, however, the flame begins to vibrate and alters in character. The vibrations become more and more intense, the flame swinging backwards and forwards with oscillations of increasing amplitude. Then one or other of two things happens; either the flame is extinguished, or it goes forward with an exceedingly great and constant velocity, producing the most violent effects. The new condition thus set up is termed "*Detonation*," and the forward movement of the flame is called the "*Explosion Wave*."

The discovery of "*detonation*" in gaseous mixtures was made simultaneously by M. Berthelot and MM. Malard and Le Chatelier, in the year 1881; Berthelot proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and

that for the same gaseous mixture under given physical conditions it always has a constant value. In this connection I would mention Professor H. B. Dixon's exhaustive researches on the "*rates of explosion*" of gaseous mixtures, which have extended in so many ways our knowledge of explosive combustion.

*Experiment I.*—Perhaps the best illustration of the outward difference between ordinary "*inflammation*" and "*detonation*" is afforded by the case of a mixture of carbonic oxide and oxygen in their combining ratios. When ignited in an open tube 4 or 5 inches long, the mixture burns quietly with the familiar blue flame. Far otherwise is it, however, when a long column of the mixture is fired in a leaden coil, where the brief initial period of *inflammation* is succeeded by the *explosion wave*, which dashes onwards through the gases at a rate of 1700 metres (about a mile) per second with shattering effect.

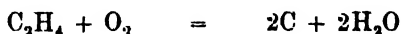
Another notable feature of "*detonation*" is the extremely short duration of the flame. In the course of some experiments carried out under Professor Dixon's direction, it was found that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas does not exceed  $\frac{1}{20000}$ th part of a second. But short as this time is, it is something like a million times longer than the interval between successive molecular collisions in a gaseous mixture.

The question of how a hydrocarbon burns, that is to say, precisely how it is attacked by the oxygen, has been the subject of much discussion during the past fifteen years. A hydrocarbon is a compound of the two combustible elements, carbon and hydrogen, and in a sufficient supply of oxygen, both of these are ultimately burnt to carbon dioxide and steam, respectively. Thus, for example, in the case of ethane :—



On kinetic grounds, however, it seems inconceivable that the passage from the initial system of ethane and oxygen to the final system of carbon dioxide and steam can be immediate and direct. It is, therefore, universally recognised that the process involves a number of successive stages. But opinion has been sharply divided as to the nature and sequence of these stages, and I will now endeavour to put before you the main points in dispute. They may be conveniently summarised under three heads.

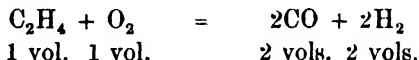
1. During the greater part of last century the belief prevailed that the hydrogen is much the more combustible of the two elements of a hydrocarbon, and that consequently when combustion occurs in a limited supply of oxygen, the hydrogen is preferentially burnt, as follows :—



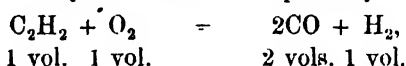
Who was the author of this view, or what was originally its experimental basis, is not quite clear, but it received the active support of two such eminent authorities as Thomas Graham and Michael Faraday, and for fifty years it was regarded as one of the most certain articles of chemical faith. Its final overthrow by Dixon and Smithells in the year 1892, caused no small stir in chemical circles.

2. The second theory originated with Kersten in 1861, who as the outcome of experiments on the explosion of a mixture of ethylene and electrolytic gas, asserted that "before any portion of the hydrogen is burnt, all the carbon is burnt to carbonic oxide, and that the excess of oxygen then divides itself between the carbonic oxide and the hydrogen." In other words, Kersten attempted to substitute the idea of the preferential burning of carbon for that of the preferential burning of hydrogen. His views, however, received no serious attention until they were revived and endorsed by Dixon and Smithells in 1892.

The chief experimental basis for this theory is the behaviour of ethylene and acetylene when exploded with their own volume of oxygen. More than a century ago, Dalton found that a mixture of equal volumes of ethylene and oxygen yields mainly carbonic oxide and hydrogen on explosion, without any separation of carbon, in conformity with the equation :—

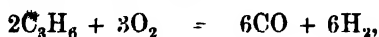


This fact, after being overlooked for nearly eighty years, was rediscovered by Dixon in 1891; moreover, a few years later, when it was proved that acetylene behaves in a precisely similar manner—



the advocates of the theory were able to claim a strong body of evidence in support of their case.

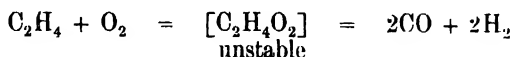
3. But the idea of a "*preferential*" combustion, whether of carbon or of hydrogen, seemed repugnant to well-established principles concerning the nature and conditions of chemical interactions in gaseous systems. Moreover, whilst the assumption of a *direct* passage from an initial system of ethylene and oxygen,  $\text{C}_2\text{H}_4 + \text{O}_2$ , to the system carbonic oxide and hydrogen,  $2\text{CO} + 2\text{H}_2$ , implied a simple trans-action from the kinetic standpoint, an extension of the idea to the case of such a hydrocarbon as propylene—



would at once raise serious difficulties.

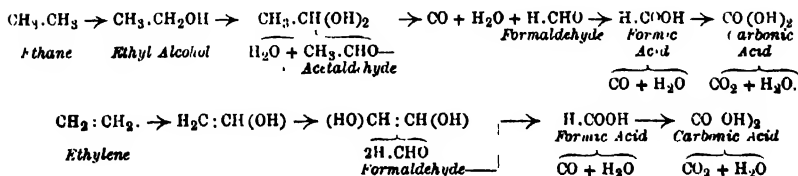
It therefore remained to consider whether the solution of the

problem might not lie in the assumption of an initial *association* of the hydrocarbon and oxygen forming an unstable "oxygenated" molecule, which subsequently rapidly decomposes. Thus, for example, the changes involved in the explosive combustion of an equimolecular mixture of ethylene and oxygen might conceivably be represented somewhat as follows :—



Many years ago, indeed, Professor H. E. Armstrong, suggested that the combustion of a hydrocarbon takes place under the conjoint influence of water and oxygen, and involves the successive formation of intermediate "*hydroxylated*" molecules, which at high temperatures rapidly decompose into simpler products. Little notice was taken of his suggestion at the time, but recent researches have shown that "*hydroxylated*" molecules are probably formed, even in flames, although I think it doubtful whether water vapour is an essential factor in the process.

The researches recently carried out at the Manchester University, have covered the entire range of conditions under which hydrocarbons can be burned, from the slow flameless combustion discovered by Davy, right up to the extreme conditions of detonation. An exhaustive study of the slow combustion of methane, ethane, ethylene, and acetylene, at temperatures between 250° and 400° C., afforded decisive evidence against the preferential burning, whether of carbon or of hydrogen. Large quantities of aldehydic intermediate products were isolated, and the balance of evidence was decidedly in favour of the "*hydroxylation*" theory, with the proviso, however, that the oxygen is directly active. Finally, the following scheme was put forward for the slow combustion of ethane, and ethylene at 250° to 350° C.

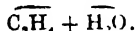
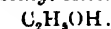


Translated into words, this means that, in the case of ethane, the initial oxidation product is probably *ethyl alcohol*  $\text{C}_2\text{H}_5\cdot\text{OH}$ . The alcohol has not, indeed, been actually isolated during the slow combustion at 300° C., chiefly because it is much more rapidly oxidised

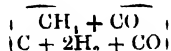
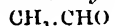
under these conditions than is ethane itself; it is, however, formed in quantity when ethane is oxidised by means of ozone at  $100^{\circ}\text{C}$ . The second stage involves the rapid oxidation of the alcohol to the unstable  $\text{CH}_3 \cdot \text{CH}(\text{OH})_2$ , which at once decomposes into steam and *acetaldehyde*. The *acetaldehyde* is in turn burnt to carbonic oxide, steam, and *formaldehyde* (possibly through the unstable  $\begin{smallmatrix} \text{HO} \cdot \text{C} \cdot \text{H} \\ \text{HO} \cdot \text{C} \cdot \text{O} \end{smallmatrix}$ ), and finally the *formaldehyde* is burnt to steam and oxides of carbon, probably through *formic acid* and *carbonic acid*.

As the temperature rises, the intermediate products become more and more unstable, and to an increasing extent decompose into simpler products, which then undergo independent oxidation. Thus *ethyl alcohol* decomposes into ethylene and steam, *acetaldehyde* either into methane and carbon monoxide, or into carbon, hydrogen, methane, and carbon monoxide, according to the temperature, and *formaldehyde* is resolved into carbon monoxide and hydrogen, as follows:—

*Ethyl Alcohol*



*Acetaldehyde*



*Formaldehyde*



With the extension of the research to the conditions existing in hydrocarbon flames and explosions, it became increasingly evident that the mechanism of combustion is essentially the same above as below the ignition point. I do not mean, of course, that the phenomena observed at low temperatures, in slow combustion, are exactly reproduced in flames, but rather that the result of the initial molecular encounter between the hydrocarbon and oxygen is probably much the same in the two cases, namely, the formation of an "oxygenated" molecule. At the higher temperatures of flames, secondary thermal decompositions undoubtedly come into operation at an earlier stage, and play a more important *role* than in slow combustion, but they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence of it. I am aware that there are eminent critics who, whilst admitting the validity of these views as applied to slow combustion, hesitate to accept entirely their extension to explosive combustion. They find it difficult to believe that such compounds as ethyl alcohol, acetaldehyde, formaldehyde, and the like, which are undoubtedly very unstable at high temperatures, can possibly be formed in flames. But surely this objection involves some confusion of thought as to the factors which govern the formation and stability of chemical compounds; the fact that a substance cannot permanently exist at a given temperature

does not justify the assertion that it cannot be formed at that temperature by the operation of factors which are not concerned in its decomposition. Therefore, I am not prepared to admit that because the acetaldehyde molecule does not long remain intact at high temperatures, it necessarily follows that it cannot be brought into actual existence as the result of the interaction of ethane and oxygen in flames.

Professor Smithells, in his recent presidential address to the chemical section at the British Association (1907), expressed his dissent from my views, as applied to flames, on the ground that "The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances. . . ." To this I would reply, that whilst the isolation of (say) acetaldehyde in the slow oxidation of ethane is not *by itself* sufficient proof of its transitory formation in the explosive combustion of the hydrocarbon, yet if it can be demonstrated, not only that the facts of explosive combustion can be *best* interpreted on the assumption of its formation, but that, so far as can be judged at present, no other interpretation can be advanced, and, moreover, that aldehydes are actually produced in flames, then it may be justly claimed that the assumption is well founded, and that the onus of its experimental disproof rests with the sceptics.

Having thus, I hope, explained the main issues involved in the controversy, I shall now proceed to perform a series of experiments on the explosive combustion of acetylene, ethylene, and ethane, some of which are crucial as regards the rival theories under discussion.

*Experiment II.*—I have here three cylindrical bulbs of stout borosilicate glass (capacity = about 60 c.c.), fitted with firing wires, hermetically sealed, and containing respectively equimolecular mixtures of each of the three hydrocarbons with oxygen, that is to say, mixtures corresponding to  $C_2H_2 + O_2$ ,  $C_2H_4 + O_2$ , and  $C_2H_6 + O_2$ , respectively.

Now, according to the theory of the preferential combustion of carbon, these mixtures should on explosion, yield nothing but carbonic oxide and hydrogen, without any separation of carbon, or formation of steam, as follows:—

					$p_2/p_1^*$
(a)	$C_2H_2 + O_2 = 2CO + H_2$	.	.	.	1.5
(b)	$C_2H_4 + O_2 = 2CO + 2H_2$	.	.	.	2.0
(c)	$C_2H_6 + O_2 = 2CO + 3H_2$	.	.	.	2.5

\* The symbols  $p_1$  and  $p_2$ , used in this and subsequent tables, denote the initial and final pressures of the *cold* original mixture and gaseous products (dry) at constant volume and at the same temperature.

On firing the mixtures, it is at once evident that something very like this does happen in the cases of (a) and (b). There is absolutely no deposition of carbon, and no appreciable condensation of steam in the cold products. Far otherwise is it, however, in the case of the bulb containing the mixture  $C_2H_6 + O_2$ . A lurid flame fills the vessel, accompanied by a black cloud of carbon particles, and a close inspection of the cold bulb will reveal a considerable condensation of water. The pressure ratio  $p_2/p_1$  is approximately 1.5, and an analysis of the gaseous products would prove the presence of about 10 per cent. of methane. The bulb will now be opened, rinsed out with water, and the formation of aldehydic products demonstrated by means of Schiff's reagent. It is clear that these results are wholly inconsistent with the theory of the preferential burning of carbon.

As it is obviously impracticable for me to complete the experiment by analysing the gaseous products before you, I will draw your attention to the following tabulated results of three similar experiments carried out some time ago.

TABLE I.—RESULTS OF EXPERIMENTS ON INFLAMMATION IN SEALED GLASS BULBS.

Original Mixture.		$C_2H_2 + O_2$	$C_2H_4 + O_2$	$C_2H_6 + O_2$						
$p_1$		352 mm	545 mm	746 mm.						
$p_2$		508 „	1053 „	1148 „						
$p_2/p_1$		1.44	1.93	1.54						
* Composition of gaseous products.	$CO_2$	0.75	0.30	4.20						
	$CO$	67.10	50.00	33.55						
	$C_2H_2 + C_2H_4$	nil	nil	2.75						
	$CH_4$	1.55	1.70	10.85						
	$H_2$	30.60	48.00	48.60						
		C	H	O	C	H	O	C	H	O
Units in original mixture		352	176	176	545	545	272	746	1119	376
Units in gaseous products		352	171	175	547	541	267	621	854	241
Difference		Practically nil.			Practically nil.			125	265	135

Did time permit, I could easily demonstrate to you by other similar experiments, that the *outward* difference here revealed between the burning of ethylene and that of ethane extends to all the other gaseous olefines and paraffins: that is to say, whereas mixtures of olefines and oxygen corresponding to  $C_nH_{2n} + \frac{n}{2} O_2$  on explosion



yield mainly carbonic oxide and hydrogen, without separation of carbon, mixtures of paraffin and oxygen corresponding to  $C_nH_{2n+2} + \frac{n}{2} O_2$  yield carbon, oxides of carbon, methane, hydrogen, and steam, all in considerable quantities. Are we then to conclude that there is some peculiarity about the constitution or combustion of an olefine which induces a preferential burning of its carbon, whilst the corresponding paraffin is burnt in an entirely different way? The following experiment will show that such a view cannot for a moment be entertained.

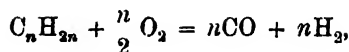
*Experiment III.*—I will now fire a bulb containing a mixture of 60 per cent. of ethylene and 40 per cent. of oxygen (i.e.  $3C_2H_4 + 2O_2$ ). As might be expected, the flame is accompanied by a large deposition of carbon, but what is of greater importance still is the fact that a considerable amount of water is also formed. The full significance of this experiment may be gathered from the following data.

Original mixture  $\left\{ \begin{array}{l} C_2H_4 = 59.65 \text{ per cent.} \\ O_2 = 40.35 \text{ } \end{array} \right. \quad \begin{array}{l} p_1 = 562 \text{ mm.} \\ p_2 = 816 \text{ } \end{array} \quad p_2/p_1 = 1.45$

Gaseous products  $CO_2 = 2.5, CO = 37.2, C_2H_2 + C_2H_4 = 6.4, CH_4 = 6.5,$   
 $H_2 = 47.4 \text{ per cent.}$

	C	H	O
Units in original mixture . . . . .	670	670	227
Units in gaseous products . . . . .	482	572	172
Difference . . . . .	188	98	55

I think it will be now admitted that such an experiment as this completely destroys the foundations of the theory of the preferential burning of carbon. As I have already stated, the original experimental basis of the theory, was the behaviour of an equimolecular mixture of ethylene and oxygen, yet here is proof that on closer examination the behaviour of ethylene is inconsistent with the theory. I would therefore say to those who may be inclined to cavil at my views as to the mechanism of combustion, that whatever may be the final issue of the controversy, this fact, amongst others, must be explained, namely, that whereas a mixture of an olefine and oxygen corresponding to  $C_nH_{2n} + \frac{n}{2} O_2$ , yields mainly carbonic oxide and hydrogen on explosion, in harmony with the equation—



a diminution of the oxygen below this limit at once gives rise to steam formation.

*Experiment IV.*—The next experiment is designed to illustrate the infinitely greater affinity of acetylene and ethylene as compared with that of hydrogen for oxygen at the high temperatures of flames. I have here two bulbs containing mixtures of each of these hydrocarbons with hydrogen and oxygen corresponding to  $C_2H_2 + 2H_2 + O_2$  and  $C_2H_4 + H_2 + O_2$ , respectively, and I will ask you to contrast the behaviour of these with that of the equimolecular mixture of ethane and oxygen,  $C_2H_6 + O_2$ , which was exploded a few minutes ago. It should be noted that whilst all three mixtures contain the same relative proportions of carbon, hydrogen and oxygen, they differ in respect of the proportions between the combined carbon and hydrogen. Asking you to bear in mind how the equimolecular mixture of ethane and oxygen on explosion gave rise to a black cloud of carbon and a considerable formation of water, I will now fire the other two mixtures. You will observe that in neither case has there been any deposition of carbon, and an inspection of the cold bulbs will show that little or no steam formation has occurred. In fact, the hydrocarbon has been burnt to carbonic oxide and hydrogen, leaving the hydrogen absolutely untouched by the oxygen, as the following detailed results show (Table II.).

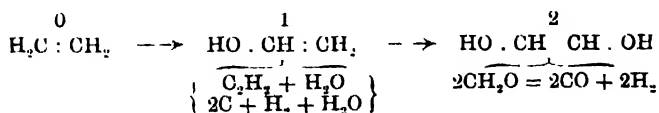
These experiments have an important bearing on the chemistry of flames. Hydrogen is usually considered as one of the most combustible of gases, but here we see it pushed to one side by the all-powerful hydrocarbon, as though it were so much inert nitrogen. This at once raises another question which has lately been occupying my attention. Ever since Davy's experiments on flame, the combustibility of hydrogen has been considered to be superior to that of methane; this, however, cannot be true in regard to slow combustion, since it can be easily proved that between  $300^\circ$  and  $400^\circ C$  methane is oxidised at a far faster rate than hydrogen. Nevertheless, I have recently observed facts which incline me to think that possibly it may be true in regard to flames. If further investigation confirms this opinion, it will be necessary to enquire into the cause of the peculiar relative inertness and stability of methane as compared with other gaseous hydrocarbons when subjected to the action of oxygen at high temperatures.

It does not I think impose too great a strain on the imagination to picture the probable mechanism of combustion in hydrocarbon flames, and for this purpose ethylene and ethane may be taken as typical examples. It may be assumed that, with the possible exception of methane, the affinity of a hydrocarbon for oxygen is so great at high temperatures that the initial stage of its combustion takes

TABLE II.—EXPERIMENTS ON INFLAMMATION IN SEALED GLASS BULBS.

Original Mixture.		$C_2H_4 + H_2 + O_2$			$C_2H_2 + 2H_2 + O_2$		
$p_1$		508 mm.			584 mm.		
$p_2$		750 "			658 "		
$p_2/p_1$		1.49			1.22		
% Composition of gaseous Products.	$CO_2$	0.35			0.2		
	$CO$	39.60			39.8		
	$C_2H_2 + C_2H_4$	1.25			nil		
	$CH_4$	3.65			0.2		
	$H_2$	55.15			59.8		
		C	H	O	C	H	O
Original mixture . . .		341	505	168	267	400	133
Gaseous products . . .		346	478	151	262	394	131
Difference . . .			27	17	Negligible.		

precedence of all other chemical phenomena in flames. This is probably true of the propagation of flame through explosive mixtures of hydrocarbons and oxygen. In the special case of a stream of a hydrocarbon burning in air, partial decomposition may occur in the innermost regions of the flame, where the supply of oxygen is very limited, before combustion begins. But, in general, whenever the hydrocarbon and oxygen are brought together at high temperatures, their mutual affinities will prove superior to any disruptive forces which would otherwise break down the hydrocarbon. It is probably not so much the original hydrocarbon as its hydroxylated molecule which decomposes in flames; the sudden increase in the internal energy of the hydrocarbon molecule, consequent upon its initial association with oxygen, would render the resulting hydroxylated molecule extremely unstable, and, in default of its immediate further oxidation, it would speedily decompose. The explosive combustion of ethylene may, therefore, be represented by the following scheme—

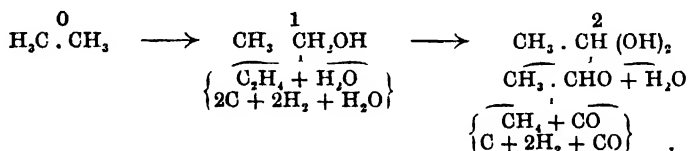


In a sufficient supply of oxygen, the transition from the original hydrocarbon to the *dihydroxy* state is probably so rapid that no breaking down of the ethylenic structure occurs in passing through the initial *monohydroxy* stage. Indeed, it is conceivable that under

the extreme conditions of detonation the passage from 0 to 2 may be effected in a single molecular impact. The *dihydroxy* derivative would at once break down into carbon monoxide and hydrogen, *via* formaldehyde.

But when the oxygen supply is reduced below the equimolecular proportion, it is evident that the initial *monohydroxy* derivative cannot all be oxidised to the *dihydroxy* stage; some of it would, therefore decompose, partly into acetylene and steam, and partly also into carbon, hydrogen, and steam, together with some methane.

In a similar manner, the combustion of ethane would involve the rapid passage through *ethyl alcohol* to *acetaldehyde* and *steam*, with subsequent decomposition of the aldehyde into carbon, hydrogen, methane, and carbonic oxide, with the proviso that a reduction of the oxygen supply below the equimolecular proportion, would bring about in some measure the decomposition of the alcohol into ethylene and steam, etc., at stage 1.



But the cases of ethane and ethylene are typical of all other hydrocarbons, so that it may be said that, in general, the mechanism of explosive combustion involves, (1) the initial formation and subsequent decomposition of hydroxylated (or "oxygenated") molecules; (2) in a sufficient supply of oxygen, the independent oxidation of the decomposition products; (3) in an insufficient oxygen supply, the subsequent breaking down of unsaturated hydrocarbons, interactions between carbon and steam, or between oxides of carbon, hydrogen, and steam, the final system depending on the amount of available oxygen, the temperature of the flame, and the rate of cooling.

*Experiment V.*—The influence of different rates of cooling of the flame on the final system may be illustrated by firing an equimolecular mixture of ethane and oxygen in two glass vessels, having approximately the same volume, but widely different surface areas. For this purpose I have selected (1) a tube about 1 metre long and 2 cm. internal diameter, and (2) a globe of 8.5 cm. internal diameter. Both these vessels have the same volume (about 300 c.c.), but the surface area of the tube is very nearly 3 times that of the globe. It is therefore to be expected that, in consequence of the more rapid cooling of the flame, there will be a greater accumulation of the primary combustion products in the case of the tube experiment. On comparing the results of the two explosions, it is at once evident that more water and less carbon have been produced in the case of the tube; moreover, the pressure ratio  $p_2/p_1$ , is 1.45 as com-

pared with about 1.75 in the globe experiment, and an examination of the products would show that the lower ratio is accounted for by the much greater survival of acetylene, ethylene, and aldehydic products in the tube experiment. These facts, which are set forth in the following table, are in complete harmony with the hydroxylation theory.

TABLE III.—INFLAMMATION OF AN EQUIMOLECULAR MIXTURE OF ETHANE AND OXYGEN

		A. In Long Tube.			B. In Large Globe.		
		701 mm.			685 mm.		
		1018 "			1187 "		
		1 45 "			1.73 "		
% Composition of Gaseous Products	$p_1$						
	$p_2$						
	$p_2/p_1$						
	CO <sub>2</sub>	4.20			3.40		
	CO	34.80			36.10		
	C <sub>2</sub> H <sub>2</sub>	5.00			0.15		
	C <sub>2</sub> H <sub>4</sub>	2.65			7.25		
	CH <sub>4</sub>	8.85			53.05		
	H <sub>2</sub>	44.50					
		C	H	O	C	H	O
Original mixture		694	1041	354	678	1017	346
Gaseous products		643	738	220	558	805	255
Difference		51	303	134	120	212	91
% Difference		7.6	29	37.8	18	20	27.5

*Experiment VI.*—The experiments I have so far shown you, refer more particularly to the initial period of "*inflammation*" in explosive combustion, that is to say, to the conditions ordinarily prevailing in hydrocarbon flames. The question may be asked whether or not the views I have advanced are applicable to the extreme conditions of "*detonation*" or of explosions under high initial pressures. The question may be put in the following form: Is there any experimental evidence of discontinuity between "*inflammation*" and "*detonation*" as regards the nature and sequence of the chemical changes involved? or, Is the hydrocarbon attacked by oxygen in an entirely different way in explosive combustion at high pressures, or in the explosion wave, to what it is in ordinary flames? This question can, I think, best be answered by a consideration of the behaviour of an equimolecular mixture of ethane and oxygen under these extreme conditions.

It is difficult to set up detonation in this mixture; the gases

must be fired at an initial pressure of about  $1\frac{1}{2}$  atmosphere in a stout leaden coil of about 1 inch internal diameter. Even then, it is necessary to start the explosion wave in a special firing piece containing electrolytic gas under pressure. I therefore regret that, owing to the special arrangements requisite for success, it is not possible to make the experiment to-night. I will, however, give you the results obtained on detonating the mixture in my laboratory, but before doing so, I will carry out an experiment on the explosion of the gases at an initial pressure of 15 atmospheres.

The cylindrical steel bomb on the table is part of an apparatus recently installed in the Fuel and Metallurgical Laboratories of the University of Leeds for investigations on gaseous explosions under high pressures. The bomb is about a foot long with an external diameter of 4 inches, and the central cylindrical explosion chamber is 8 inches long by 1 inch in diameter. It has been tested by hydraulic pressure up to 2000 atmospheres, and has been repeatedly used for experiments with mixtures of hydrocarbons and oxygen at initial pressures of as much as 40 atmospheres. The bomb is now connected, through a valve at the top, with a standard Bourdon gauge, and contains an equimolecular mixture of ethane and oxygen at a pressure of 15.8 atmospheres. The valve will now be closed, and the mixture fired by means of an electrical arrangement in the special firing piece.

All that is audible of the explosion is a sharp click, and on opening the valve connecting with the gauge again, the final pressure of the cold products of explosion is recorded. After applying the necessary correction for the "dead space" in the gauge connections, but the final "corrected" pressure is as nearly as possible 30.8 atmospheres, corresponding to a ratio  $p_2/p_1 = 1.93$ . I would now direct your attention to the tabulated results of a similar bomb experiment carried out a few weeks ago at Leeds at an initial pressure of 25 atmospheres, and also at the same time to those of another experiment in which the gases were detonated in a lead coil at an initial pressure of  $1\frac{1}{2}$  atmosphere.

In both these experiments carbon was deposited, and it is evident also, that steam was formed. The ratio  $p_2/p_1$ , was as nearly as possible 2.0 instead of the 2.5 required by the theory of the preferential combustion of carbon. Moreover, a notable feature of the results is the presence of as much as 7 per cent. of methane among the products of the experiment at 25 atmospheres; the fact that so much methane survived when all other hydrocarbons were battered to pieces during the explosion (no traces of either acetylene or ethylene being found in the products) is a remarkable testimony to its relatively great stability at the highest temperatures of explosion flames. There is no evidence in these experiments, of any real discontinuity between the chemical phenomena of ordinary "inflammation" and those of "detonation." The higher temperatures, and more violent conditions in

TABLE IV.—RESULTS OF EXPLOSION OF AN EQUIMOLECULAR MIXTURE ETHANE AND OXYGEN UNDER HIGH PRESSURES.

		A. Detonation in Lead Coil.			B. Explosion in Steel Bomb.		
		$P_1$ $P_2$ $P_2/P_1$			25.2 atms. 51.7 2.05 "		
% Composition of Gaseous Products.	CO <sub>2</sub>	1.80			2.6		
	CO	39.10			37.2		
	C <sub>2</sub> H <sub>2</sub>	0.90		} 1.40 }	nil		
	C <sub>2</sub> H <sub>4</sub>	0.50					
	CH <sub>4</sub>	7.70			7.0		
	H <sub>2</sub>	50.00			52.2		
		C	H	O	C	H	O
Original mixture . . .		1186	1779	587 mm.	25.35	38.0	12.55 atms.
Gaseous products . . .		1151	1507	488 "	24.50	34.6	11.05 "
Difference . . .		35	272	99 "	0.85	3.4	1.5
% Difference . . .		3	15	17	3.4	9	12.0

"detonation" are responsible for the more complete breaking down of unsaturated hydrocarbons, and a greater "unburning" of steam by carbon, but there is probably no difference as regards the mode in which the hydrocarbon is attacked by the oxygen in the two cases.

I therefore believe, that, so far as our present knowledge goes, the views I have put forward, afford a simple and consistent interpretation of hydrocarbon combustion, whether it be the slow flameless kind discovered by Davy, or the more complex phenomena of ordinary flames so wonderfully expounded by him, or finally the extreme conditions characteristic of the explosion wave.\*

\* I desire to acknowledge the devoted help rendered to me in the conduct of these investigations by the following research students of the Manchester University: Messrs. R. V. Wheeler, W. E. Stockings, G. W. Andrew, Julien Drugman, and H. Henstock.

[W. A. B.]

Friday, April 10, 1908.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. D.C.L.  
LL.D. F.R.S., in the Chair.

PROFESSOR SIR J. J. THOMSON, M.A. LL.D. D.Sc. F.R.S. *M.R.I.* ;  
Professor of Natural Philosophy, Royal Institution.

*The Carriers of Positive Electricity.*

THOUGH the ordinary cathode rays are the most conspicuous of the rays spreading out from the cathode in a vacuum-tube, there are other rays mixed with them, which as Goldstein\* and the writer† showed long ago are not appreciably deflected by weak magnetic fields. The very complete study of the region near the cathode made by Goldstein, the results of which are described in a paper read before the Physical Society of Berlin,‡ has led him to distinguish five kinds of rays besides the cathode rays. Recent experiments made by Villard§ and the author|| have shown that some of these rays are deflected in electric and strong magnetic fields, and the direction of the deflexion indicates that they carry a positive charge of electricity. The fact that these positively charged rays travel with high velocities away from the cathode, and thus against the direction of the electric force, makes the investigation of their properties a very interesting problem, and I have lately made a series of experiments with the object of obtaining some information as to their nature and origin.

The tube used in the first series of experiments is represented in Fig. 1. A is a perforated electrode through which rays can pass on their way to the phosphorescent screen S covered with Willemite; the rays on their journey to the screen traverse strong electric and magnetic fields, the former produced by charging the plates L M to different potentials and the latter by placing the tube between the poles of a powerful electromagnet. From the deflexions which these produce on the rays, the velocities and values of  $e/m$  for the rays can be determined in the usual way. B is a flat electrode at the other end of the tube; this electrode is carried by a stopper working in a ground-glass joint, and can be rotated about a vertical axis. C is an auxiliary electrode at the side of the tube. D is a side tube in which

\* Verhandl. d. Deutsch. physik. Gesellsch. iv. p. 228, 1902.

† Proc. Camb. Phil. Soc. ix. p. 248. ‡ Republished Phil. Mag. Mar. 1908.

§ Comptes Rendus, cxliii. p. 678, 1906. || Phil. Mag. xiv. p. 869, 1907.



a metallic obstacle is placed at the end of a rod, this end is fastened to a closed glass vessel containing a piece of iron. By moving this vessel along D by means of a magnet, the obstacle can either be inserted in the line of fire of the rays coming from B and passing down the hole in A, or withdrawn into the tube; the obstacle is in metallic

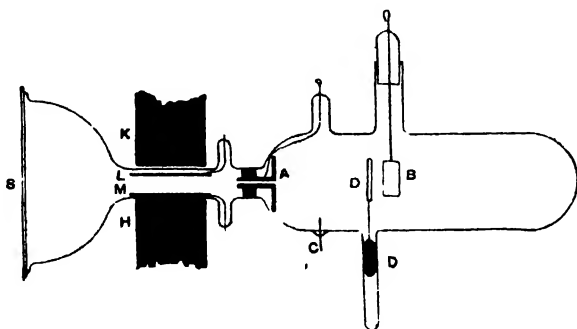


FIG. 1.

connexion with a wire leading out of the tube, so that it can be used as a cathode if required. The discharge through the tube was produced in some cases by a large induction-coil, in others by a Wimshurst machine.

If the stopper carrying the electrode B were turned so that the normal to the electrode coincided with the axis of the tube A, or made only a small angle with it, and if B were made cathode and a discharge sent through the tube, then in addition to the cathode rays other rays passed through the tube in A and excited phosphorescence on the screen. The direction of the deflexions of the phosphorescence under electric and magnetic forces showed that these rays were charged with positive electricity.

If A were made cathode, the ordinary Canalstrahlen produced bright phosphorescence on the screen. The first point investigated was to make sure that the positive rays observed when A was anode, were not due to reversals of the induction-coil making A at times a cathode and sending ordinary Canalstrahlen down the tube. Very simple observations, however, showed that this could not be the explanation. In the first place, the positive rays still passed down the tube when A was disconnected from the coil and the auxiliary electrode C used as an anode; secondly, A being connected with the coil, the rays down the tube disappeared when B was twisted round, so that the normal to its plane made a considerable angle with the axis of the tube; and thirdly, the rays down the tube were stopped when the obstacle in the side tube was pushed forward so as to be in the line between the cathode and the aperture in the anode.

The next point investigated was to see whether the effect might

not be due to A acting at times as a cathode in virtue of the negative charge given up to it by the cathode rays starting from B. That this is not the explanation is proved by the following experiments. When the cathode rays were diverted by a magnet so that they no longer fell upon A, the brightness of the phosphorescent patch due to the positive rays going down the tube in A was not appreciably diminished, although the tendency for A to become cathode must have been almost entirely removed. The conclusions drawn from this experiment were confirmed by the results obtained when the obstacle in the side tube was used as a cathode instead of B. When the obstacle was not pushed far enough across the tube for its normal to pass down the tube in A, no positive rays passed down the tube, but as soon as the obstacle had advanced into such a position that its normal went down the aperture in A, the phosphorescence on the screen due to the positive rays appeared. The contrast between the brightness of the phosphorescence when the normal to the obstacle went down the hole in A and when it did not was very sharp, though there was very little variation in the number of cathode rays striking against the anode as a whole. These experiments show that the positive rays under discussion are not due to reversals of the induction-coil nor to the negative electrification of A by the bombardment of cathode rays, but that they originate at the cathode and travel away from it down the tube.

By means of the rotating cathode B we can determine whether the positive rays coming from the cathode are emitted normally to its surface, or whether, like some of the rays observed by Goldstein, they come off in all directions. When the normal to the cathode went down the tube in A, a plentiful supply of positive rays went down the tube. When the cathode was rotated, the phosphorescence due to the positive rays did not immediately disappear, although it became very much fainter; it could, however, be detected until the normal to the cathode made an angle of about  $15^{\circ}$  with the axis of the tube. The positive rays under discussion appear to follow much the same path as the cathode rays, for it was found that the angle of rotation required to prevent these getting down the tube was much the same as that required to extinguish the phosphorescence due to the positive rays.

#### *Properties of these Positive Rays.*

These rays get exceedingly faint at very low pressures, and cease to be observable at pressures when the Canalstrahlen are still quite bright. It is probably due to this that I have never been able to observe the resolution of the phosphorescence, under the action of electric and magnetic forces, into separate patches as in the case of Canalstrahlen when the pressure is low.\* The spot of phosphorescence

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\* Phil. Mag. xiii. p. 561, 1907.

due to the positive rays coming out in front of the cathode is, under the action of electric and magnetic deflexion of the rays, drawn out into a continuous band, even when the pressure is such that the phosphorescence due to the Canalstrahlen shows well-developed patches. In the case of the Canalstrahlen, there are some rays whose deflexion shows that they are negatively charged and have a mass comparable with that of the positive rays. We find, too, in the case of the rays travelling in the opposite direction to the Canalstrahlen, that a considerable number of them are negatively charged particles, indeed I think the proportion of the negative to the positive is greater in this case than in that of the Canalstrahlen. I have observed cases in which the phosphorescence due to the negatively charged particles was little, if at all, less than that due to the positively charged ones.

A large number of determinations were made, by the method described in my first paper,\* of the velocity and values of  $e/m$  for these rays; in consequence of the spot of phosphorescence being drawn out into a band, the values of  $e/m$  ranged continuously from 0 to a maximum value.

Two tubes were used for this purpose, in one of them (fig. 1) the electrode B was connected with a stopper ground into the tube, one side of the electrode was aluminium, the other calcium; by turning the stopper either side could be made to face the tube A, down which the rays passed. LM are parallel plates, which can be connected with a battery of storage-cells; when this is done, rays passing between the plates are acted on by a strong electric field. S is the screen at the end of the tube; H, K the pole-pieces of the electro-magnets. C is a wire fused into the tube, to serve as an electrode, thus allowing A to be insulated or connected with one or other of the electrodes at will. The dimensions of the parts of the tube which affect the deflexions of the phosphorescence are as follows:—

Distance between the plates L and M = 0.45 cm.

Length of these plates . . . . = 3.8 cm.

Distance between the screen and the  
end of the plates . . . . = 4.0 cm.

If  $V$  is the potential in volts between the plates,  $e$  the charge,  $m$  the mass, and  $v$  the velocity of the rays,  $D$  the deflexion due to the electrostatic field, we can easily prove that

$$\frac{e}{mv^2} = \frac{D}{5 \times 10^9 V}$$

While if  $d$  is the deflexion due to the magnetic field when a current of 1 ampere is passing through the coils, it was found by the method described † that

$$\frac{e}{mv} = 2.8 \times 10^4 \frac{d}{V}$$

\* Phil. Mag. xiii. p. 561, 1907.

† Loc. cit.

From these equations the following determinations of  $e/m$  and  $v$  were made ; the value of  $V$  was 420 volts.

Tube filled with Air.			
D.	$d$	$e/m$	$v$
·5	1·4	$10^4$	$2 \times 10^8$ cm./sec.
·4	1·1	$\cdot 78 \times 10^4$	$2 \times 10^8$ "
·5	1·4	$10^4$	$2 \times 10^8$ "
·45	1·3	$\cdot 96 \times 10^4$	$2\cdot1 \times 10^8$ "
·4	1·4	$1\cdot25 \times 10^4$	$2\cdot5 \times 10^8$ "
·4	1·3	$1\cdot08 \times 10^4$	$2\cdot8 \times 10^8$ "
·3	1·1	$1\cdot04 \times 10^4$	$2\cdot6 \times 10^8$ "
Mean		$1\cdot01 \times 10^4$	
Tube filled with Hydrogen.			
·7	1·7	$1\cdot05 \times 10^4$	$1\cdot8 \times 10^8$ cm./sec.
·4	1·3	$1\cdot08 \times 10^4$	$2\cdot3 \times 10^8$ "
·6	1·5	$\cdot 96 \times 10^4$	$1\cdot7 \times 10^8$ "
·4	1·3	$1\cdot08 \times 10^4$	$2\cdot8 \times 10^8$ "
Mean		$1\cdot04 \times 10^4$	

The other type of tube (Fig. 2), in which there were no auxiliary electrodes, had the following dimensions :—

Distance between the plates L and M . . . = 0·4 cm.

Length of plates . . . . . = 4·0 cm.

Distance between screen and plate . . . = 3·5 cm.

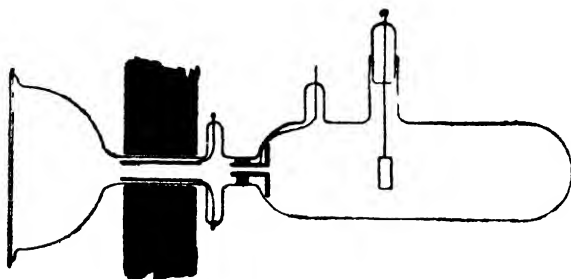


FIG. 2.

Hence if  $V$  is the potential-difference in volts between the plates, and  $D$ , as before, the deflexion in the electrostatic field,

$$\frac{e}{mv^2} = \frac{D}{5\cdot5 \times 10^9 V}$$

The magnet had been readjusted and furnished with new pole-pieces. If  $d$  was the magnetic deflexion, it was found that when 1 ampere was the current through the coils

$$\frac{e}{mv} = \frac{d}{4.5 \times 10^4}.$$

With this tube the following values of  $e/m$  and  $v$  were obtained for the positive rays proceeding from the cathode in the opposite direction to the Canalstrahlen. The value of  $V$  was 400 volts.

Tube filled with Air.			
D	$d$	$e/m$	$v$
·4	1·7	$83 \times 10^4$	$2.2 \times 10^8$ cm./sec.
·3	1·6	$9 \times 10^4$	$2.6 \times 10^8$ "
·5	1.9	$.72 \times 10^4$	$1.7 \times 10^8$ "
·5	2.0	$9 \times 10^4$	$2.0 \times 10^8$ "
·1	1·8	$9 \times 10^4$	$2.2 \times 10^8$ "
·2	1·3	$.9 \times 10^4$	$3.2 \times 10^8$ "
·4	1·7	$83 \times 10^4$	$2.2 \times 10^8$ "
Mean . .		$85 \times 10^4$	
Tube filled with Helium.			
·5	20	$9 \times 10^4$	$2.0 \times 10^8$ cm./sec.
·5	22	$1.08 \times 10^4$	$2.2 \times 10^8$ "
·5	21	$1 \times 10^4$	$2.1 \times 10^8$ "
Mean . .		$.99 \times 10^4$	

The deflexions of the Canalstrahlen in the same tube were also observed: this could easily be done by making the tube A the cathode. It was found that the structure of the Canalstrahlen was more complicated than that of the retrograde positive rays, the former showing two types of rays, characterised by values of  $e/m$  in the ratio of 2 to 1: the latter showed only one type of ray, this type coinciding, however, both as to value of  $e/m$  and the velocity with the type of Canalstrahlen rays having the maximum value of  $e/m$ . Some of the retrograde rays, as well as some of the Canalstrahlen, are deflected in a direction which shows that they carry a negative charge, and that their mass is comparable with that of the positively charged particles. I have determined the value of  $e/m$  and the velocity of these negative constituents of the retrograde rays, and find that the

value of  $e/m$  for the negative particles is numerically equal to that of  $e/m$  for the positive ones; while the velocity of the negative ones is slightly, but only slightly (about 15 per cent. in my experiments), less than that of the positive ones.

*Experiments with Goldstein's Double Cathodes.*

Goldstein \* found that when the cathode consists of two parallel plates in metallic connexion, rays other than the cathode rays proceed from the space between the plates. If the plates are triangles, Goldstein found that a pencil of easily deflected cathode rays starts from the middle points of the sides, while pencils of undeflected rays start from the corners of the triangle. The difference in the character of the rays can be strikingly shown by using helium in the discharge-tube, when the rays from the corners are red and those from the sides blue. I have examined the electric and magnetic deflexion of these rays, using for the purpose a tube such as that shown in Fig. 3.

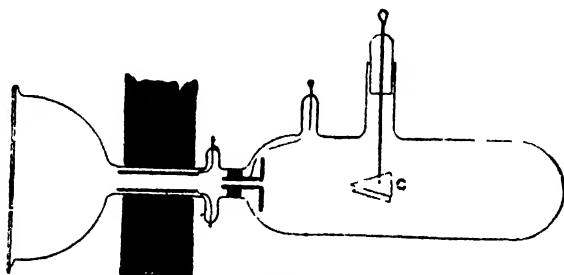


FIG. 3.

The cathode consists of two parallel triangles, and is carried by a stopper working in a ground-glass tube. By turning the stopper the different parts of the triangular cathode could be brought opposite to the opening in the tube and the distribution of the rays round the triangle studied. I found that this distribution depended a good deal upon the pressure of the gas in the discharge-tube. At all the pressures I tried, I found that the maximum emission of ordinary cathode rays was along the line starting from the middle points of the sides; at the higher pressures, this was the only direction in which the cathode rays could be detected; at very low pressures, however, rays could be detected starting from the corners of the triangle, as well as from the middle points of the sides; few, if any, however, were given out in any intermediate position. With regard to the positive rays, I found at all the pressures I tried that these

\* Loc. cit.

streamed off from both the corners and the middle points of the sides, there were but few in any intermediate position; the most abundant stream came, as was the case for cathode rays, from the middle points of the sides, but the disproportion between the streams from the corners and from the sides was nothing like so great for the positive as it was for the cathode rays; so that the ratio of the quantity of the positive rays to the quantity of cathode rays was greatest at the corners of the triangle.

I also measured the velocity and the value of  $e/m$  for the positive rays. I found that this was the same whether the rays came from the corners or from the sides, and the same as that of one type of Canalstrahlen (the type for which  $e/m = 10^4$ ), which went down the tube when A was made cathode. In the case of the positive rays coming from the triangular cathode, often only a small fraction were at all affected by electric and magnetic forces, by far the larger portions were quite undeflected by these forces; so that the phosphorescence of the screen when the magnetic force was applied to the tube presented the appearance of a bright central undeflected patch with a faintly luminous tail.

We can, I think, explain this distribution of the rays from the triangular cathode on the view that there is a reciprocity between the cathode rays and the positive rays of the following kind. The corpuscles in the cathode rays are due to the impact of positive ions at or near the cathode, while the positive rays are due to the impact of the corpuscles at some distance from the cathode. Let us consider now what happens when the lines of electric force in the neighbourhood

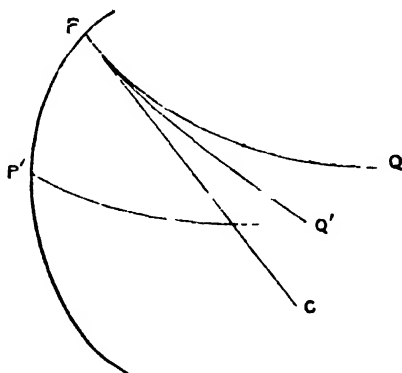


FIG. 4.

of the cathode are curved as in Fig. 4. A corpuscle starting along the normal from P would on account of its inertia not follow the line of force PQ but some path P'Q' between PC and PQ, PC being the normal to the cathode. If, now, the corpuscle produces a posi-

tive ion at  $Q'$ , this ion as it moves up to the cathode will not follow the path  $Q'P$  but some such path as  $Q'P'$ , striking the cathode at  $P'$ , and producing a cathode ray at  $P'$ . Thus the positive particle, if it strikes the cathode at all, will not give rise to a cathode ray to replace the one which produced it, but a ray starting from some other region. If, however, the line of force starting from  $P$  were a straight line, the positive particle produced by the ray at  $P$  would strike the cathode at  $P$ . When the discharge is in a steady state the number of corpuscles coming from *any region* must be proportional to the number of positive particles falling on that region. Now this will be the case when and only (except perhaps in very special cases) when the positive rays which strike the region are those produced by the corpuscles coming from it. For this to happen, the lines of force from that region must be straight lines. In the case of the triangular cathode there are six regions where the lines of force are straight, the middle points of the sides and the corners; and it is therefore from these regions that we should expect the discharge to be concentrated; and inasmuch as the region over which the lines are approximately straight is much greater at the middle points of the sides than at the corners, we should expect the maximum discharge to come from the middle point of the sides.

### *Magneto-Cathodic Rays.*

Among the rays which sometimes occur near the cathode are some observed by Villard,\* and called by him magneto-cathodic rays. These rays occur when the discharge-tube is placed in a strong magnetic field; they are in the direction of the lines of magnetic force, and when subject to an external electric field they are displaced in a direction at right angles to the electric and also to the magnetic force. Ions moving through a medium in which they are under the action of electric and magnetic forces, and which resists their motion with a force proportional to their velocity, would behave exactly in this manner. For, just as a stone falling through a resisting medium moves at first with nearly uniform acceleration but after a time settles down into a state where the velocity is constant and equal to what is known as the limiting velocity, so ions, when exposed to electric and magnetic forces and to a resistance proportional to their velocity, will after a time settle down to a state where the velocity is uniform. The time required to reach this state is inversely proportional to the resistance when the velocity is unity and directly proportional to the mass of the ion. I have shown in my "Conduction of Electricity through Gases"† that when the ions have reached this state, and the magnetic

\* Comptes Rendus, cix. p. 42, 1905.

† Second edition, p. 106.



force  $H$  is so large that  $Hu_0$  is large compared with unity,  $u_0$  being the velocity acquired by an ion when unit force acts upon it, and inversely proportional to the pressure, then the ions move nearly along the lines of magnetic force, but have a small component in the direction at right angles to both the electric and magnetic forces. In these respects they resemble Villard's magneto-cathodic rays; the ions, however, would carry electric charges, while Villard could detect no charge when the magneto-cathodic rays entered a Faraday cylinder. It is perhaps possible that the absence of charge may have been due to the rays making the gas round the Faraday cylinder so good a conductor of electricity, that no appreciable charge could accumulate in the cylinder.

*On the Method by which the Retrograde Rays acquire their Velocity.*

We have seen that the velocity of those positive rays which move away from the cathode, and which are, when under observation, free from the influence of the electric field in the tube, is practically the same as that of the Canalstrahlen which have moved up to and then passed through the cathode. This result is remarkable, for in the latter case the action of the electric field which produces the discharge in the tube would increase the velocity of a positively charged particle, while in the former it would diminish it. The fact that the velocities in the two cases are very much the same suggests, at first, the suspicion that the electric field may not be accountable for any considerable portion of the velocity in either case, and that perhaps the particles forming these rays may, like the  $\alpha$  particles given out by radioactive substances, start with a high initial velocity, much higher than they could acquire under the electric field. If we refer to the table of velocities, we shall see that there is not, in the different experiments, much variation in the velocity of the particles; these are always  $2 \times 10^8$  cm./sec., and could be generated by a fall through a potential difference of about 20,000 volts. We must not, however, attach too much importance to the constancy of the velocity, for the range of pressure over which we can make accurate observations on the retrograde rays is very limited. For when the pressure gets very low, and the discharge requires a high potential-difference to send it through the tube, the rays are not bright enough to be observed; while if the pressure is more than a small fraction of a millimetre, the rays either do not reach the screen, or when they do reach it are so diffuse that the phosphorescent patch is not definite enough for its position to be measured with accuracy. And although even rough measurements show that at these high pressures the velocity of the particles is less than when the pressure is low, we should not be justified without further evidence in concluding

that the initial velocity was less, for before reaching the screen the rays have had to make a long journey through the gas, and if the pressure is high, they will in their journey lose more of their velocity than when the pressure is low.

To test whether or not the velocity of the rays was due to the electric field, I tried the following experiments :—

In the first experiment, a piece of wire gauze was placed about 2 mm. in front of the perforated electrode of the tube represented in Fig. 2 and well insulated from it; the gauze was used as the cathode, and measurements of the velocity of the particles were made (1) when the perforated electrode was connected with the gauze, (2) when it was connected with the anode. In the second case, a particle if it retained its charge during the whole of its path, would in its journey between the gauze and the perforated electrode be at least as much retarded as it had been accelerated before reaching the gauze, and any velocity it possessed after passing through the perforated electrode must have been acquired from sources independent of the electric field; while in the first case its velocity would be measured by the electric field in the tube. On trying the experiment, it was found that though the Canalstrahlen were not nearly as bright in the second case as in the first, they were still quite perceptible, and that the velocity of those which got through was the same as the velocity of those reaching the screen in the first case. The fact that a large proportion of the rays are stopped by connecting the perforated electrode with the anode, while those which get through are not affected, shows that the velocity of the majority of them is not great enough to travel against the potential-difference between the electrodes; while the fact that some get through without diminution of velocity, indicates that when they are passing between the gauze and the perforated electrode, they are for the moment electrically neutral and without charge, and that they re-acquire, by losing a corpuscle, a positive charge after passing through the opening in the electrode by collision with the molecules of the gas. The following experiment shows in perhaps a simpler way than the preceding one that some of the Canalstrahlen are uncharged during a portion of their path. The perforated cathode (Fig. 5) was wedge-shaped, the angle of the wedge being about  $27^\circ$ , the diameter of the cathode was 2 cm., the aperture through which the Canalstrahlen passed was about 5 mm. from the sharp end, the length of the path of the rays from one side of the cathode to another was about 2.5 mm. A flat piece of wire gauze was fixed parallel to the upper face of the cathode (the face most remote from the anode), and insulated from it: the distance of the gauze from the cathode was about 3 mm. The Canalstrahlen travel at right angles to the lower face A B of the cathode. If the wire gauze is connected with the anode, and if the particles in the Canalstrahlen are charged, they will after passing through the cathode be acted on by a force which has a component at

right angles to their direction of projection : thus if they are positively charged they will be bent to the right, if they are negatively charged to the left, while if they are uncharged they will be undeflected. The path of the rays when the pressure of the gas is not too low, can

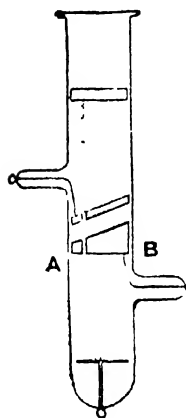


FIG. 5.

readily be traced by the luminosity they produce in the gas as they pass through it. On trying the experiment, it was found that when the gauze was connected with the anode the path of the few rays which got through the gauze was a straight line, coinciding in direction with their path before passing through the cathode. An easy way of seeing this is to connect by means of a key the gauze in quick succession with the anode and the cathode, when it is easily seen that though the Canalstrahlen are much more numerous in the latter case than in the former, the paths of those which do get through are identical, so that even when the gauze is connected with the anode some of the rays get through the space between *cd* and *cf* without suffering any deflexion, showing that they must be uncharged as they pass through this region. It is thus evident that a considerable number of the positively charged Canalstrahlen lose their

positive charge by attracting when in the neighbourhood of the cathode a negatively electrified corpuscle ; the mass of the corpuscle is so small in comparison with that of the particles forming the Canalstrahlen, that the addition of the corpuscle will not materially reduce the velocity of the Canalstrahlen. These rapidly moving uncharged particles will soon get ionized by collision, and by losing a negatively electrified corpuscle again become positively charged.

In my first paper on the positive rays,\* I showed that at not too low pressures the appearance presented by the phosphorescence on the screen indicated that many of the particles in the Canalstrahlen were positively charged for only a portion of their path ; the experiments just described are very direct evidence of this effect.

Again, at not too low pressures the Canalstrahlen are accompanied by negatively electrified particles having masses and velocities equal to those of the positive particles ; the negatively electrified particles in my experiments always being less numerous than the positive ones, in most cases very much so, in others the difference was not very great. We should expect the negatively electrified particles to be less numerous than the positive ones, since they would more readily lose their charges by collision.

I think that the positive rays which travel away from the cathode

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\* Phil. Mag. xiii. p. 561.

arise in the same way as the negative rays which accompany the Canalstrahlen. Let us consider what happens to the Canalstrahlen as they approach the cathode. When they reach the cathode some of them, as we have seen, get neutralized there, some will go further than this, and by gathering another corpuscle will become negatively electrified; those negatively electrified ones will, however, be repelled from the cathode, and under the action of the electric field will acquire a velocity of the same order as that acquired by the positive particles in their approach to the cathode. The rapidly moving electrified particles will in their course through the gas soon lose corpuscles by collision and thus become positively electrified, forming the positive rays which come from the cathode. Such rays, however, on the view just given start their journey with a negative charge.

The Canalstrahlen and the positive retrograde rays are not found with all types of discharge; thus, in the type of discharge sometimes called the flash discharge, which occurs when a condenser of large capacity is earthed through the discharge-tube, the discharge passes as a column of uniform luminosity stretching from one electrode to the other, and there is no dark space in the neighbourhood of the cathode. In this case I have never been able to detect positive rays of any kind, either in front of or behind the cathode.

It is important to distinguish between the positive ions to be found in a gas, ionized by Röntgen rays and not exposed to electric fields strong enough to give to them very high velocities; and the positive ions which, like those in the Canalstrahlen, have very great kinetic energy. For between the positive charges and the molecules there are forces comparable in intensity to those which exist between the atoms of different elements having the greatest chemical affinity for each other. Thus, unless the positive ions possess more than certain amount of kinetic energy, combination will go on with great rapidity and positively charged aggregates will be formed. If, however, the positive ions are moving with great rapidity, they will be in a state analogous to a gas at a very high temperature, and at these very high temperatures chemical combination does not take place. We have seen that the particles in the Canalstrahlen have a velocity of the order of  $2 \times 10^8$  cm./sec. With a velocity such as this their kinetic energy would be equal to the mean kinetic energy of the molecules of a gas at a temperature of many hundred thousand degrees absolute; and though, as I have shown,\* a positive ion might be expected to combine with a corpuscle if its velocity were but a little less than this, it would not be likely to do so with an uncharged molecule where the attraction would be very much less. If we take the case of a positive ion of mass  $m$  projected with a velocity  $V$  at right angles to the line joining it with a molecule of

\* Conduction of Electricity through gases, 2nd edit. p. 360.

mass  $M$ , and at a given distance from it, the condition that the ion should be able to get away from the molecule is that

$$mV^2 > \frac{M}{m + M}$$

should be greater than a certain quantity depending on the force between the molecules and the ion and apsidal distance between them. Now if the force were independent of the mass of the molecule, we see that it would require a greater value of  $mV^2$  to separate the ion from the molecule, when  $M$  is small compared with  $m$ , than when it is large. Thus if the kinetic energy of the ions were gradually to diminish say by collisions with the molecules, then if there were molecules of different masses in the gas through which the Canalstrahlen are moving, combination would occur first with the molecules of smallest mass, while the heaviest molecules would be the last to combine. The lightest molecules would thus have the first pick of the ions, which would therefore tend to be absorbed by the lightest gases. The force between an ion and a molecule is proportional to the volume of the molecule; and if the volume of a molecule were to increase as rapidly as its mass, the preceding considerations would not be valid. We have every reason, however, to believe that the changes in the volume of the molecules are not comparable with the changes in the masses: that, for example, the volume of a molecule of oxygen, instead of being sixteen times that of a molecule of hydrogen, is hardly more than twice, so that the increase in the forces exerted by the heavier molecules is not sufficient to counteract the influence of the increased mass.

*The Nature of the Positive Ions in different Gases when the Ionization has settled into a steady state.*

The Canalstrahlen are formed in very intense electric fields, and the kinetic energy which they possess tends to prevent them combining with the molecules and corpuscles around them; they are thus under quite different conditions from the ordinary ions produced in a region where the electric force is small or absent, for these have time before being removed from the field to enter into combination with the molecules, the system of molecules and ions getting into a steady state if the source of ionization is constant. The difference between this case and that of the Canalstrahlen may be compared with the difference between the state of a mixture of different chemical substances after they have entered into combination and settled into a state of equilibrium and when they were first mixed. I thought that it would be interesting to determine the values of  $e/m$  for the ordinary ions simultaneously with the determination of  $e/m$  for the Canalstrahlen in the same discharge-tube. The method used to

determine  $e/m$  for the ordinary ions was as follows. A tube represented in Fig. 6 was sealed on to the tubes such as have already been described in connexion with the determination of  $e/m$  for the Canalstrahlen. B is an ionization chamber, the gas in it being ionized by cathode rays coming down through the tube C which was connected with the earth. The cathode was at D in front of the tube, the anode in a side tube F. Three parallel electrodes, L, M, N, were put in the ionization chamber. The first, L, was a plate at the top of the tube; the second, M, near the bottom. Of the tube was a piece of wire gauze about a millimetre above N, which was the top of an

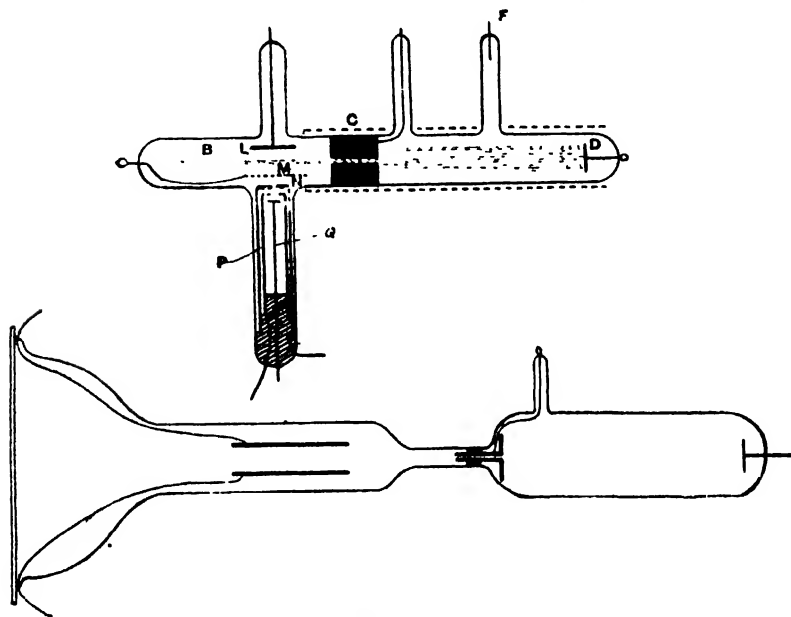


FIG. 6.

earth-connected cylinder, with a small hole 0.9 mm. in diameter bored through the centre, the thickness of this plate was 1.6 mm. By means of these electrodes ions could be collected and some of them sent through the hole with a definite and known velocity. Suppose for example we wish to send a stream of positive ions through the hole. A small difference of potential (in our experiments generally that due to two Leclanché cells) was maintained between the plates L M, L being at the higher potential. The electric field produced in this way caused a stream of slowly moving positive ions to pass downwards through the gauze; by means of a potential divider any potential-difference between 10 and 800 volts could be established

between the gauze and the top of the cylinder, the gauze being positive to the cylinder. The ions collected by the upper plates thus entered into a much stronger field which gave to them a velocity much greater than that with which they entered it, so that when they passed through the hole they were all moving with practically the same velocity.

Beneath the top of the box there was an insulated Faraday cylinder (P) connected with a Wilson electroscope. The distance between the top of the cylinder and the bottom of the plate was 1 mm. in one piece of apparatus, 0.5 mm. in another; the diameter of the hole in the Faraday cylinder was 2.3 mm. Beneath this hole there was a metal disk insulated and connected with another Wilson electroscope; the plane of the disk was parallel to N and thus at right angles to the undeviated path of the ions, the axis of the hole in N passed through the centre of the disk. The part of the tube below N was placed between the poles of a powerful electromagnet, the lines of magnetic force being at right angles to the undeviated path of the ions, and parallel to the direction of the cathode rays. To protect the cathode rays coming from D from the magnetic field, a deep cutting was made in one of the poles of the electromagnet and the portion from C to D of the tube placed in this and then covered over with layers of soft iron. This tube was sealed on to the tube T of the kind already described, for the determination of  $e/m$  for the Canalstrahlen.

If the ions travelled without deviation parallel to the axis of the tunnel in N, they would all strike against the disk Q, and the Faraday cylinder would not receive any charge. If, on the other hand, they were very much deflected by the magnetic field, they would all strike against the Faraday cylinder and the disk would not receive any charge. If we measure the charges received by the disk and the Faraday cylinder during any time, the ratio of the charges will be the ratio of the number of ions which strike against the disk to the number striking against the cylinder. The readings of the electroscopes do not give us directly the charges received by the systems to which they are attached, but the potentials to which these systems are raised. We can, however, if we know the ratio of the potentials easily deduce that of the charges. For let  $E_1, V_1$  be the charge and potential of the Faraday cylinder,  $E_2, V_2$  the corresponding quantities for the disk.

Thus if the  $q$ 's represent coefficients of capacity, we have

$$\begin{aligned} E_1 &= q_1 V_1 + q_{12} V_2 \\ E_2 &= q_{12} V_1 + q_2 V_2, \end{aligned}$$

so that

$$\frac{E_1}{E_2} = \frac{q_1 V_1 + q_{12} V_2}{q_{12} V_1 + q_2 V_2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

To determine the  $q$ 's by experiment we proceed as follows. Given a charge to the disk, the cylinder being insulated and uncharged, then if  $V_1'$  and  $V_2'$  are respectively the potentials of the cylinder and disk as determined by their electroscopes,

$$q_1 V_1' + q_{12} V_2' = 0, \quad \text{since } E_1 = 0.$$

Thus if  $\alpha$  is the ratio of the potential of the cylinder to that of the disk when the cylinder is uncharged,

$$q_1 = -q_{12} \frac{V_2'}{V_1'} = -\frac{q_{12}}{\alpha}.$$

Similarly, if  $\beta$  is the ratio of the potential of the disk to that of the cylinder when the disk is uncharged, we have

$$q_2 = -\frac{q_{12}}{\beta}.$$

Substituting in equation (1) we have

$$\begin{aligned} E_1 &= \beta (V_1 - \alpha V_2) \\ E_2 &= \alpha V_2 - \beta V_1. \end{aligned}$$

The quantities  $\alpha$  and  $\beta$  are very easily determined, and from this equation we can deduce the ratio of the charges when we know that of the potentials. By using two electroscopes and determining by means of them the *ratio* of the charges received by the cylinder and disk, we eliminate any irregularities that might arise from variations in the working of the coil used to produce the cathode rays which ionize the gas in the ionization chamber.

If an ion is projected through the tunnel in  $N$  along the axis of the tunnel, it will, if there is no magnetic field acting upon it, travel along a straight line and hit the disk. If there is a magnetic field its path, after getting through the hole, will be a circle, since if it is free when once it has got through the hole from any electric force, it will, however, continue to hit the disk until the radius of this circle is less than the radius of the circle passing through the hole, the edge of the disk, and touching at the hole the axis of the tunnel. If  $d$  is the distance of the disk below the hole,  $a$  the radius of the disk,  $r$  the radius of this circle is equal to  $\frac{d^2 + a^2}{2a}$ . When the radius of the path

of the ion is less than this, the ion will give up its charge to the Faraday cylinder; when it is greater than this it will give up its charge to the disk.

If  $H$  is the magnetic force acting on the ion,  $e$  its charge,  $m$  its mass, and  $r$  the radius of its circular orbit,

$$H e r = m v,$$



if  $V$  is the potential-difference between the gauze and the top of the box

$$V e = \frac{1}{2} m v^2;$$

thus

$$H^2 r^2 \frac{e}{m} = 2 V.$$

Thus when  $H$  increases through the value given by the equation

$$H^2 \left( \frac{a^2 + a^2}{2a} \right) \frac{e}{m} = 2 V, \quad . \quad . \quad . \quad . \quad (2)$$

there ought to be a large increase in the ratio of the charge on the Faraday cylinder to that on the disk. If the pencil of ions coming through the hole were indefinitely thin, and if all the ions travelled with the same velocity in the same direction, the transference of the charge from the disk to the cylinder would be quite abrupt. With a magnetic force less than a certain value, all the charge would be on the disk, while with a force greater than this all the charge would be on the cylinder. In my experiments the diameter of the hole, 0.9 mm., was a considerable fraction of the length 1.6 mm. of the tunnel, so that there was a considerable latitude in the direction of propagation of ions through the hole. This has the effect of making the ratio of the charges on the cylinder and disk change much less abruptly than if they were all projected in the same direction, since those ions which are projected towards the side of the cylinder to which they are bent by the magnetic field, will be carried to the side by a smaller magnetic force than those which are projected at right angles to the disk. When the hole is very small, the charge carried by the ions passing through it in a given time is also very small, and the potentials of the disk and cylinder change very slowly. The purpose for which these experiments were made was not so much to get accurate values of  $e/m$  for the ions as to find out whether these had masses comparable with the mass of an atom of hydrogen, or of oxygen, etc. The arrangement used was adequate for doing this, and had the advantage of giving a supply of ions which could produce measurable effects in a minute or so, thus avoiding many difficulties as to insulation which crop up when the experiments have to be extended over very much longer periods. Experiments with very much smaller holes are, however, in progress.

The strength of the magnetic field between the poles was determined by comparing the currents induced in a small coil when suddenly withdrawn from the magnetic field with the current obtained by turning an earth inductor through  $180^\circ$  in the earth's magnetic field. When the pole-pieces were 1.15 cm. apart, the magnetic forces  $H$  for different currents through the coils of the electromagnet were as follows :—

Current through Electromagnet  
in Amperes.

H.

0.5	.	.	.	.	.	.	.	1330
1	.	.	.	.	.	.	.	2570
2.5	.	.	.	.	.	.	.	4000
2	.	.	.	.	.	.	.	4900
2.5	.	.	.	.	.	.	.	5600
3	.	.	.	.	.	.	.	6000
3.5	.	.	.	.	.	.	.	6400
4	.	.	.	.	.	.	.	6660

When, as in our Faraday cylinder,  $d = 5$  mm.  $e = 2$  mm., the radius of the critical circle  $\frac{d^2 + a^2}{2a} = 0.725$  mm., we see by the application of equation (2) that if  $e/m = 10^4$ , the potential-difference  $V$  required to reduce the radius of the orbit to the critical value would, when the currents through the electro-magnets were 1, 2, 3, 4 amperes, be respectively 170, 620, 900, 1100 volts. These are the potential-differences between the gauze and the top of the cylinder  $N$  required to send the ions to the plate. The following table gives the charge acquired by the disk when the sum of the charges on the disk and Faraday cylinder was 100 for different strengths of magnetic fields; assuming that all the ions carry the same charge, these numbers represent the percentage of the ions passing through the hole which reach the disk. In the table  $V$  is the potential-difference between the gauze and  $N$  in volts,  $i$  the current through the electro-magnet in amperes, and  $n$  the percentage of ions which reach the disk. The gas in the tube was hydrogen.

	$V = 10.$	$V = 20.$	$V = 30$	$V = 40.$	$V = 50.$	$V = 60.$	$V = 80.$
$i$	$n$	$n$	$n$	$n$	$n$	$n$	$n$
1 . .	17	18.4	18	18	18	19	22.8
2 . .	18	23	23	22	22	20	19
3 . .	11	16	22	23	25	26	21
4 . .	8	9	20	22.5	25	27	26

	$V = 100.$	$V = 120.$	$V = 140.$	$V = 160.$	$V = 180$	$V = 420.$
1 . .	23	25	24	28	31	50.5
2 . .	16	17	22	14	12	12
3 . .	21	19	19	16	9	9
4 . .	25	23	21	18	15	8

On looking at the numbers we see that until the voltage exceeds 160 volts there is no appreciable difference between the number of ions going to the disk when the magnetic field is due to a current of 1 ampere, and when it is due to 2 amperes. We saw, from the preceding calculation, that a voltage of 170 volts would carry ions for which  $e/m = 10^4$  to the disk against the electric current, while

it would require about 700 volts to drive them across when the current was 2 amperes, thus the difference which sets in between the results when  $i = 1$  and  $i = 2$  at 160 volts indicates the presence of a considerable number of ions for which  $e/m = 10^4$ .

For voltages between 30 and 160 there is no appreciable difference with currents ranging from 1 to 4 amperes, while for voltages less than 30 there is an appreciable diminution in the number which get to the disk when the current through the electromagnet is raised from 1 to 4 amperes. This indicates that there are some ions which, under a voltage of say 25 volts, are stopped when the magnetic field is that due to 4 amperes, but can get across when it is due to 2 amperes. Since 1100 volts would just drive particles for which  $e/m = 10^4$  across the field due to 4 amperes, 25 volts will drive particles for which  $e/m = 10^4/(1100/25) = 10^4/44$  across this field. For the field due to 2 amperes 620 volts are required to drive particles for which  $e/m = 10^4$ , 25 volts will drive particles for which  $e/m = 10^4/(620/25) = 10^4/25$ . From the preceding results we infer the presence of ions for which  $e/m$  is between  $10^4/44$  and  $10^4/25$ . Such ions might be molecules of nitrogen or oxygen due to traces of air in the discharge-tube; these, however, are only a small fraction of the whole number of ions. The pressure of the hydrogen in this case was about 0.003 mm. It is necessary to work at pressures so low that the mean free path of the ion is large compared with the distance  $d$ .

Let us now compare the results obtained when the apparatus had been repeatedly filled with oxygen obtained by heating permanganate of potash in a tube fused on to the discharge-tube, running the coil with the gas at the pressure when the discharge passes most easily, and then filling and repumping; the oxygen on its way from the permanganate to the discharge tube went through a worm immersed in liquid air to free it from any traces of water vapour given off from the permanganate. No hydrogen lines could be detected in the spectrum. The Faraday cylinder had been taken down between this experiment and the preceding one, and slightly altered so that the radius of the critical circle in this case when  $d = 4$ ,  $a = 2.5$ , is 0.47 cm., hence the potentials required to force ions for which  $e/m = 10^4$  across to the disk when currents 1, 2, 3, 4 amperes flow through the coils of the electromagnet are respectively 72, 270, 400, and 480 volts. The pressure of the oxygen was 0.009 mm.

The following (see Table on next page) are the results of the experiments,  $n$  as before being the percentage of ions which reach the disk.

The figures in this case are quite different from those for hydrogen. We see that for voltages over 100 the charge on the disk is not appreciably diminished when the current through the electromagnet is raised from 1 up to 4 amperes; this shows that the number of ions with masses comparable with those of a hydrogen atom is too

	V = 10.	V = 15.	V = 20.	V = 25.	V = 30.
$\iota$	$n$	$n$	$n$	$n$	$n$
1 . . .	75	82	81	81	80
2 . . .	56	62	68	72	72
3 . . .	36	43	50	58	61
4 . . .	28	27	43	50	56

	V = 40	N = 100.	V = 200.	V = 300.	V = 400.
1 . . .	82	81	81	81	81
2 . . .	78	80	80	80	81
3 . . .	68	78	76	79	80
4 . . .	63	76	79	80	80

small to be detected, for such ions under a field of 100 volts would have been able to make their way to the disk against a magnetic field due to 1 ampere, but not that due to 2 amperes or more; thus if these had been present in any considerable number, the number reaching the disk when  $\iota = 1$  would have been appreciably greater than when  $\iota = 2$ .

The fact that 20 per cent. under these voltages reach the Faraday cylinder is due, I think, to the obliquity of the ions as they come through the hole, and to the diffusion they suffer in passing through the gas. Under the smaller voltages the effect of the magnitude of the magnetic field is very apparent; thus until the voltage is above 20, the majority of them are stopped by a field of 4 amperes, indicating that the mass of the majority of the ions is not greater than  $480/20$  or 24 times the mass of an atom of hydrogen. In fact that the majority of the ions have masses comparable with that of the molecule of oxygen, and are not aggregates of several molecules.

Though the preceding list shows that the number of ordinary hydrogen ions in this gas was too small to be detected, yet when the Canalstrahlen produced in a tube in direct connexion with the one in which the ionization occurred were investigated they were found to be well developed, and to give exactly the same value for  $e/m$  as when the apparatus had been filled with hydrogen, as in the experiments already discussed.

By measuring the relative numbers of ions carried to the cylinder and the disk by different voltages against a constant magnetic field we can readily estimate the relative amounts of heavy and light ions in the gas. Indeed I think that by using a very small hole in the plate N a very fair analysis of the gas in the ionizing chamber might be made. Thus suppose the magnetic field were that due to 3 amperes through the coils of the electromagnet; then with apparatus of the dimensions used in one of the experiments the ions for which  $e/m = 10^4$  would not reach the disk until  $V = 900$ , while those for

which  $e/m = \frac{1}{2}10^4$  would reach it when  $V = 450$ , those for which  $e/m = \frac{1}{16}10^4$  when  $V = 56$ , those for which  $V = \frac{1}{32}10^4$  when  $V = 28$ . Thus for ions of different atomic weights the stages are well separated, and the relative numbers of the ions of the different kinds could be determined. With the comparatively large hole used in the experiments described above it was quite easy to observe the gradual diminution in the number of the lighter ions, as each dose of oxygen was supplied to the tube and then pumped out. This method of analysis is applicable at pressures far below those at which even spectrum analysis is available.

By reversing the potentials in the ionization chamber we can collect and send through the opening in the plate negative ions and corpuscles which are present in large numbers in the gas. The corpuscles, on account of their small mass, are prevented from reaching either the Faraday cylinder or the disk by a comparatively small magnetic force, and then only negative ions get through to the conductor. The proportion of these reaching the disk and cylinder with changes in the electric and magnetic fields show variations of a similar character to those observed for the positive ions.

The relative rates at which the cylinder or disk charged up according as positive or negative ions were supplied to them from the ionization chamber was determined. When the magnetic field was weak the rate of charging was much more rapid with negative than with positive ions; this was due to the excess of corpuscles in the ionization chamber; when, however, the magnetic field was strong enough to stop the corpuscles, the rate of charging under potential-differences of the order of about 200 volts was about the same for the negative as for the positive ions, while with smaller differences of potential, say 25 volts, the rate of charging with negative ions was only about  $\frac{1}{6}$  of that with positive. The positive ions seem, in the ionization chamber, to be moving more rapidly than the negative, for with no electric field in that chamber both cylinder and disk acquire a positive charge when the magnetic field is strong.

With the apparatus we have been describing we can measure simultaneously the values of  $e/m$  for the ions and the Canalstrahlen in the same vessel, and the experiments we have described show that we can get a complete change in the character of the ions without any change in the nature of the Canalstrahlen; this is, I think, strong evidence that the particles composing the Canalstrahlen are the same from whatever source they may be derived.

It might, however, be urged that although the tube might be cleared of hydrogen to begin with, this gas might be driven by the discharge out of the cathode and that this might be the source of the Canalstrahlen, and I have noticed a phenomenon which at first sight suggests this view. I have observed that under some conditions there is a lag amounting in some cases to half a minute or so between starting the discharge and the appearance of the phosphor-

escence due to the canal-rays ; this might be explained by supposing that it takes time to liberate sufficient hydrogen to produce appreciable Canalstrahlen. I have made many experiments on this lag and these show that it has no special connexion with hydrogen, but is due to an alteration in the pressure of the gas produced by the discharge. It is well known that the Canalstrahlen are only well developed when the pressure in the tube is between certain limits. It is only when the initial pressure is near to, but outside, one of these limits that the lag occurs, and then the alteration in pressure which occurs when the discharge passes may accumulate until the pressure is brought within the required limits. That this, and not the introduction of hydrogen rather than any other gas, is the explanation of the lag is I think proved in the following experiments. If the presence of hydrogen were all that is wanted for the Canalstrahlen, then the lag should not occur when the tube is filled with hydrogen : we find that the lag occurs when the tube is filled with hydrogen, as well as when great precautions have been taken to remove this gas from the tube. Again, in a tube from which hydrogen has been removed and the lag is well developed, the admission of a small quantity of dry air will remove the lag just as effectively as the admission of hydrogen. When once the lag has been got rid of it is necessary to give the tube a long rest from the discharge before it returns. The fact that the lag may be destroyed by admitting a small quantity of gas shows that it is due to the alteration in pressure and not to a change produced by the discharge in the surface of the electrode. This can also be proved in the following way : two discharge-tubes A and B are connected together and with the pump, and the pressure is adjusted so that both A and B show the lag ; then if the discharge is sent through A until the lag disappears from that tube, it will be found to have simultaneously disappeared from B, though no discharge has been running through this tube.

It is somewhat remarkable that we do not, when the tube is filled with oxygen, get any trace in the Canalstrahlen of particles having masses comparable with those of the ions in oxygen. For though such ions would not be formed in very intense electric fields, there are places in the discharge-tube where the electric field is weak, as, for example, outside the cathode dark space ; we might expect positive ions to be formed in these regions, and then dragged by the electric field up to and through a perforated cathode mingling with the Canalstrahlen. The reason that we get no evidence of these oxygen ions in the Canalstrahlen is, I think, as follows : Let A be a positive ion, B a corpuscle, and let the relative velocity of A and B at the instant under consideration be at right angles to A B and equal to  $V$ . Then it is easy to show that A and B will not part company if  $\frac{mV^2}{2}$

is less than  $\frac{e^2}{AB}$ , where  $m$  is the mass and  $e$  the charge of the cor-

puscle,  $M$  the mass of the ion being supposed very large compared with  $m$ . Thus if the relative velocity falls below a certain value the ion and the corpuscle will form a neutral doublet and will cease to be a possible constituent of the Canalstrahlen. If the ion is moving much more rapidly than the corpuscle, then  $V$  will be the velocity of the ion, and we see that the smaller this velocity the more likely is it to have its charge neutralized.  $M$  being the mass of the ion  $\frac{1}{2} M V^2 = P e$ , where  $P$  is the potential-difference moved through by the ion, thus the ion will be neutralized unless  $P > \frac{M}{m} \cdot \frac{e}{AB}$ . Thus

to protect a heavy ion, for which  $M_1$  is large, from being neutralized it must be subject to a much stronger electric field than would be necessary for a light ion; thus, if there were a mixture of different gases in the discharge-tube, the ions formed from the lighter gases would persist longer than those formed from the heavier ones.

An illustration of this result is furnished by the fact that, as I showed in the paper,\* the only ions besides those of hydrogen which can be observed in the Canalstrahlen are those of the next highest gas helium, which, when the discharge passes through helium, can be observed in the Canalstrahlen without difficulty.

The places where the neutralization of the positive ions by the corpuscles takes place will be either quite close to the cathode or when the cathode is perforated in the region behind the cathode; for in front of the cathode where the positive ions are produced, though the velocity of these ions will be small, since they are in a feeble electric field, yet the corpuscles which have come from the cathode will have passed through a great potential-difference and will have a very high velocity; thus the relative velocity of the positive ions and the corpuscles will be very large. Quite close to the cathode the velocity of the corpuscles will be very small, and though the velocity of the ion will be much greater than in the former case, yet since the mass of the ion is so much greater than that of the corpuscle, the velocity acquired by the ion under the same potential-difference will be small compared with that acquired by the corpuscle, so that the relative velocity of the two close to the cathode will be much less than at a greater distance in front of it, so that combination is much more likely to occur near to the cathode, or if the cathode is perforated behind it.

If the forces between a small positive ion and an uncharged molecule are independent of the atomic weight of the molecule, or only increase slowly as the atomic weight increases, then such an ion is more likely to attach itself to a light molecule than to a heavy one; for we can show that the condition that the ion and the molecule should separate is that

$$\frac{M M' V^2}{M + M'}$$

\* Phil. Mag. ser. 5, xiii. p. 561.

should be greater than a certain quantity depending only on the force between the systems and their distance apart when nearest together.  $M$  is the mass of the ion,  $M'$  that of the molecule, and  $V$  the relative velocity of the two at the abscidal distance. If  $M'$  is very large compared with  $M$  the condition is that  $M v^2$  should be greater, while if  $M'$  were equal to  $M$ , the condition is that  $\frac{1}{2} M v^2$  should be greater than the same quantity; thus in the second case the ion would take twice as much energy to get free as in the first, and so would be more likely to combine with the molecule.

### *Nature of Ionization by Cathode Rays.*

If, as seems most probable, the positively charged particles are produced from the ionization of the gas by cathode rays, the study of the processes by which this ionization is accomplished may be expected to throw considerable light on the nature of the positive rays. When a gas is ionized by cathode rays, secondary cathode rays are generated, and the author has recently shown \* that the maximum velocity of the secondary rays is independent of the velocity of the primary rays. A comparison of the velocity of the secondary rays from gases, as determined in my experiments, with those from metals, measured by Fuchtbauer † shows that there is not much difference between the two. The velocity of the rays from gases was that due to a potential-difference of 40 volts, of those from metals that due to a potential-difference of 33 volts; the difference between these results is not greater than could be explained by errors of experiment. Thus, as far as our present knowledge goes, the velocity of a secondary cathode ray is independent both of the velocity of the primary ray and varies but little with the nature of the molecule from which the secondary ray is projected. The first result shows that the energy of the secondary ray is not acquired by a corpuscle in the primary rays striking against one in a molecule of a gas and imparting to it sufficient energy to force it out of the molecule, for if this were the case we should expect the energy of the secondary ray to vary quickly with that of the primary. Neither does it seem likely that the energy in the secondary ray is due to a general explosion of the molecule of the gas produced by a gradual accumulation of energy in the molecule from impacts with the primary rays, for then we should expect the energy in the secondary rays to depend largely on the chemical nature of the molecules.

As a working hypothesis to account for these very striking properties of the secondary rays, I would suggest that perhaps the first stage is ionization by cathode rays, may be the separation from the molecule, not of a single corpuscle, but of an electrically neutral

\* Proc. Camb. Phil. Soc. xiv. p. 510, 1908.

† Phys. Zeits. vii. p. 748, 1908.



doublet consisting of a negatively electrified corpuscle in rapid rotation round a much more massive particle with a positive charge, and that these doublets may be the same from whatever molecule they may be ejected. The secondary cathode rays are due to the subsequent breaking up of this doublet, their energy being the kinetic energy possessed by the corpuscle when rotating round the positive charge. This hypothesis would also explain the constancy of  $e/m$  in the Canalstrahlen produced from different gases.

There are many ways in which the doublet might get broken up after it had escaped from the molecule. Thus, for example, if another corpuscle, which we shall call for brevity a comet, were under the attraction of the positive particle to describe an orbit such as that shown in Fig. 7, then when the comet was in the

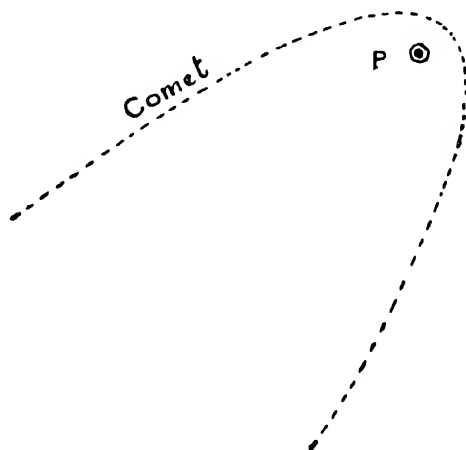


FIG. 7.

immediate neighbourhood of the positive particle, it would neutralize the attraction of this particle on the corpuscle in the doublet; thus this will move off with undiminished velocity along a straight line, and when the comet has left the system, will, if not free, be at any rate further from the positive particle than it was before, and still possessed of its original kinetic energy; if it did not get free under the influence of the first comet, a repetition of the process by other comets might liberate it from the doublet. The same effect might be produced if the positive part of the doublet came close to a gaseous molecule, which behaved like a conductor of electricity; the negative charges induced on the conductor would balance the attraction of the positive particle on the corpuscle in the doublet, and just as in the previous case, the corpuscle would be able to get off with undiminished velocity.

The questions now arise, can we get any experimental evidence of the existence of these doublets, and is it possible that such systems, if they existed, could have escaped the careful scrutiny which has been given? The second question is more easily answered than the first, for these doublets being uncharged would not possess the properties which make the positive rays or the cathode rays so noticeable; thus they would not be deflected by uniform magnetic or electric fields, and the absence of the charge might involve also a loss of the power of producing luminosity when they pass through a gas, and thus render them invisible. With regard to the first question I have made some preliminary experiments, the results of which suggest the existence in the neighbourhood of cathode of neutral systems, such as the doublets which dissociate into corpuscles and positive ions. The arrangement used in these experiments is represented in Fig. 8.

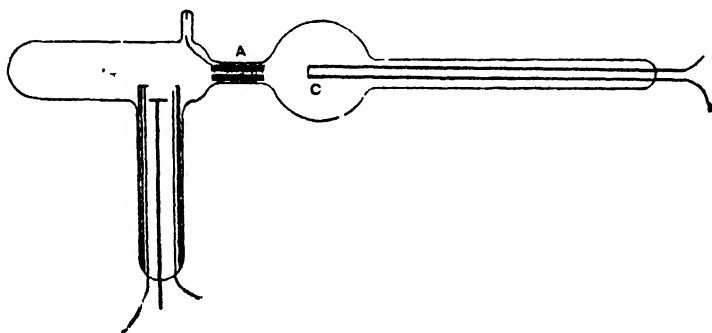


FIG 8.

The idea of the experiment was as follows. If the secondary cathode rays are produced from the primary without the intervention of the neutral doublet stage, then, as the secondary ionization is due to the secondary cathode rays, a strong electric field, arranged so as to stop the negative corpuscles forming the secondary cathode rays, ought to act as a complete screen against this ionization. If, on the other hand, there is an intermediate stage between the primary and secondary rays, and if this stage consists of neutral doublets, then some of these ought to be able to get through the strong electric field, if this is quite close to the primary rays, because it is only those secondary rays which are produced from the doublets whilst the latter are passing through the field which would be stopped; the doublets themselves will not be stopped, and if they last long enough to get through the field they ought to give rise to ionization on the other side. To test this view the apparatus represented in Fig. 8 was used. A copious supply of slowly moving primary cathode rays

was produced from the hot Wehnelt cathode C, these passed through a hole in the anode A, the anode was earthed, the primary rays passed over the top of the side tube, T; across the top of the tube were stretched two parallel pieces of wire gauze about a millimetre apart: the upper gauze was earthed, the other could be charged negatively by connecting it with the negative terminal of a battery of small storage-cells, the positive terminal of which was earthed. When the lower gauze was earthed as well as the upper, the tube was filled with the glow due to the secondary rays. When the lower gauze was charged to a negative potential of about 40 volts, this glow became exceedingly faint; but that the gas below the gauze was ionized was shown by the fact that when the negative potential of the lower gauze was increased to about 200 volts, a potential quite insufficient to produce luminosity in an unionized gas, the tube again became full of luminous glow. Thus something capable of ionizing the gas was able to traverse the strong electric field. There are two sources of ionization which have to be eliminated before we can assign this ionization to the existence of neutral systems traversing the electric field- the ultra-violet light coming from the luminous discharge in the main tube, and soft Röntgen rays produced by the slowly moving primary cathode rays. To test whether it was due to ultra-violet, a thin plate of quartz was placed over the top of the upper gauze: with this arrangement no luminosity could be detected in the side tube under the conditions as to potential and so on which gave bright luminosity in the tube when the quartz was absent. Hence I conclude that the luminosity was not due to ultra-violet light. To test whether it was due to soft Röntgen rays, taking the quartz away, I got a bright luminosity in the side tube with the primary rays passing horizontally down the tube, then by means of a magnet I bent the primary rays so that they struck the glass of the tube just above the side tube, the path of the rays being represented by the dotted line of the figure. This made the rays themselves further from the side tube, but brought the places where they struck the glass, the sources of the Röntgen rays, much nearer to that tube; so that if the ionization in the side tube were due to Röntgen rays it should be increased by the introduction of the magnet, while if it were due to the neutral doublets it would be diminished. As a matter of fact the luminosity in the side tube almost disappeared when the rays were deflected in this way, showing that it was not due to Röntgen rays, while the effect is what we should expect if the ionization were due to uncharged systems.

In the preceding experiments there is the possibility that the ionization might arise in some such way as the following. The secondary cathode rays would have to penetrate some way between the two pieces of gauze before they were stopped, and if they collided against the molecules of the gas they might ionize it: the positive ions so produced would, under the action of the electric field between

the pieces of gauze, acquire considerable kinetic energy when they reached the lower gauze, they would travel some distance after passing through before they were stopped and brought back to the gauze, and would thus have an opportunity of ionizing the gas below the gauze by collision. The negative corpuscles produced in this way would be repelled from the lower gauze and might acquire sufficient energy to produce fresh ions by collisions, and thus give rise to the luminosity observed below the gauze. To eliminate this source of ionization, a strong magnetic field was used to prevent any of the secondary cathode rays from straying into a region where they could affect the ionization in the region under observation. Two arrangements were used for this purpose. In the first, the tube with the hot lime cathode (Fig. 8) was used. The primary cathode rays were coiled up into a small bunch by means of a strong electromagnet placed just under the tube, from which the cathode rays emerge, the cathode rays in the early part of their path were screened from the effect of the magnetic force by thick iron plates. The magnetic force was strong enough to prevent the primary cathode rays, which were produced under a potential-difference of about 250 volts, from travelling more than 2 or 3 millimetres across the lines of force. The path of the rays when not under the influence of magnetic force never approached within this distance of the two pieces of gauze, and the deflexion of these rays by the magnet was away from the gauze. No luminosity could be seen close to the gauze next to the discharge-tube. Nevertheless, when the lower gauze N was at a potential of about 200 volts, the upper gauze being earthed, there was a perceptible luminous discharge in the side tube, showing that in spite of the strong magnetic field something must have passed across the gauze and ionized the gas in the side tube. A modification of this experiment was tried, in which the two pieces of gauze were connected together and with the earth, and an insulated plate connected with a charged electroscope was placed in the side tube at some distance from the gauze; the ionization in the side tube produced a leak of the electroscope. It was found that even when the primary cathode particles were coiled up by the strong magnetic field into a small bundle at the mouth of the tube from which they emerge, there was a rapid leak of the electroscope showing that the gas in the side tube was ionized. The leak was more rapid when the electroscope was positively than when it was negatively charged.

A somewhat similar experiment was also tried with the apparatus represented in Fig. 6. A magnetic field of 1200 was established between the pole-pieces, and the plates L, M, N connected with the earth, so that there was no electric field in the ionizing vessel. Under these circumstances neither the cylinder nor the disk received any electric charge when the electric discharge passed through the upper tube. The Faraday cylinder was then disconnected from the

electroscope and charged up positively to about 40 volts ; the disk now acquired a positive charge, when the cylinder was charged to - 40 volts the disk got a negative charge. This shows that the gas between the cylinder and disk was ionized, though the magnetic field prevented any negative corpuscles from entering this region.

Though we have given reasons for thinking that the Röntgen rays are not the cause of the ionization in the side tube when this is exposed to strong magnetic fields, soft Röntgen rays are produced by the impact of the primary cathode rays against the molecules of the gas in the tube. This was proved by covering the end of the side tube (Fig. 8) with thin aluminium foil and placing in the side tube behind the foil an insulated metal plate connected with a charged electroscope. The escape of electricity from this plate could not be ascribed to ionized gas making its way from the main tube into the side one, for the only channel of communication was through a long stretch of glass tubing from the main tube to the pump, and then through another long tube from the pump to the side tube ; since the opening between the main tube and the side tube was closed, it was necessary to exhaust them separately. When the primary and secondary cathode rays were well developed and the main tube filled with a bright glow, the charge from the electroscope rapidly leaked away whether it were positive or negative. The gas in the side tube is thus ionized by rays which have passed through the thin aluminium foil. The leak was, however, completely stopped when, by means of a strong magnetic field, the primary and secondary cathode rays were rolled up into a small bundle at the mouth of the tube, from which they emerge just above the aluminium foil. In this case the length of the path of the rays after coming through the tube was only 2 or 3 mm., and there was hardly any luminosity in the tube. The aluminium foil prevents the ionization in the side tube in this case, for if the foil is removed the gas, as we have already stated, is ionized.

The preceding experiments are in harmony with the view that neutral doublets are one of the stages in the process of ionization ; they must, however, be regarded as only preliminary. More extended experiments are necessary before we can be certain that the effects are not due to some very easily absorbed kind of radiation or to the diffusion of very slowly moving ions.

We have hitherto considered the case when the primary ionization was due to cathode rays, but there are reasons for thinking that similar doublets are produced when the ionization is produced by positive rays. Thus Fichtbauer\* found that the velocity of the secondary cathode rays from metals was the same whether they were produced by cathode rays or Canalstrahlen. It is sometimes argued that the much greater difficulty experienced in saturating a gas

\* Loo. cit.

ionized by  $\alpha$  particles than one ionized in any other way, shows that results of ionization are different in the two cases: this result is, however, exactly what we should expect if there were no such difference. For when a gas is ionized by  $\alpha$  rays, each  $\alpha$  particle produces an enormous number of ions, but there are comparatively few particles, and these are widely separated. Thus in a gas ionized by  $\alpha$  rays we have intense ionization in some localities and very weak ionization in others, while other methods give much more uniform ionization. Now the electric force required to saturate a gas depends upon the maximum density of ionization as well as upon the average; thus it will require a more intense field to saturate a gas ionized by  $\alpha$  particles than a gas where the total ionization is the same but the ionization is uniformly distributed through the gas. The researches of Moulin \* on the ionization by  $\alpha$  rays, show that the differences between this kind of ionization and others can be explained as arising from the want of uniformity in the distribution of the  $\alpha$  ionization.

I have much pleasure in thanking Mr. E. Everett and Mr. G. W. C. Kaye for the assistance they have given me in this investigation.

[J. J. T.]

\* Le Radium, t v March 1908.

Friday, May 1, 1908.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. D.C.L. LL.D.  
D.Sc. Pres.R.S., in the Chair.

PROFESSOR JOSEPH LARMOR, M.A. D.C.L. LL.D. D.Sc. Sec.R.S.

*The Scientific Work of William Thomson, Lord Kelvin.*

[THE material which constituted this discourse was subsequently worked up into the obituary notice of Lord Kelvin, published by the Royal Society ('Proceedings,' No. A 543, vol. 81 A, pp. i.-lxxvi.). From that source the greater part of the present report is taken textually.

The lecture was illustrated by a very complete historical collection of Lord Kelvin's scientific apparatus, utilised in part for experiments, and in part as an exhibition in the Library. This was rendered possible through the cordial co-operation of the University of Glasgow and Prof. A. Gray, F.R.S., of the firm of Messrs. Kelvin and James White, Ltd., and Dr. J. T. Bottomley, F.R.S., of the authorities of the South Kensington Museum, and other contributors.]

It would be impossible in a review of ordinary length to convey any idea of the many-sided activity by which Lord Kelvin was continually transforming physical knowledge, through more than two generations, more especially in the earlier period before practical engineering engrossed much of his attention in importunate problems which only he could solve. It is not until one tries to arrange his scattered work into the different years and periods, that the intensity of his creative force is fully realised, and some notion is acquired of what a happy strenuous career his must have been in early days, with new discoveries and new aspects of knowledge crowding in upon him faster than he could express them to the world.

The general impression left on one's mind by a connected survey of his work is overwhelming. The instinct of his own country and of the civilised world in assigning to him a unique place among the intellectual forces of the last century, was not mistaken. Other men have been as great in some special department of physical science: no one since Newton—hardly even Faraday, whose limitation was in a sense his strength—has exerted such a masterful influence over its whole domain. He might have been a more learned mathematician or an expert chemist; but he would then probably have been a less

effective discoverer. His power lay more in the direct scrutiny of physical activity, the immediate grasp of connecting principles and relations; each subject that he tackled was transformed by direct hints and analogies, brought to bear from profound contemplation of the related domains of knowledge. In the first half of his life, fundamental results arrived in such volume as often to leave behind all chance of effective development. In the midst of such accumulations he became a bad expositor; it is only by tracing his activity up and down through its fragmentary published records, and thus obtaining a consecutive view of his occupation, that a just idea of the vistas continually opening upon him may be reached. Nowhere is the supremacy of intellect more impressively illustrated. One is at times almost tempted to wish that the electric cabling of the Atlantic, his popularly best known achievement, as it was one of the most strenuous, had never been undertaken by him; nor even, perhaps, the practical settlement of electric units and instruments and methods to which it led on, thus leaving the ground largely prepared for the modern refined electric transformation of general engineering. In the absence of such pressing and absorbing distractions, what might the world not have received during the years of his prime in new discoveries and explorations among the inner processes of nature?

His scientific papers, mostly mere fragments, which overflowed from his mind, as has been said, into the nearest channel of publication, have been collected by himself up to the year 1860, in somewhat desultory manner, in four substantial volumes. In addition there are three volumes of Popular Lectures and Addresses, which are more finished products, perhaps equalled in weight and scope only by those of Helmholtz. His fertility, especially in the first dozen years from 1845 to 1856, seems to be almost without precedent. Owing to the want of systematic exposition, much of this progress was grasped only imperfectly by contemporaries, and even long afterwards; but the close attention of a few master minds, including Clerk Maxwell, and in a less degree Helmholtz, and in certain respects that of the school of scientific electrical engineers that was rising into confident power under his own inspiration, made up partially for this failure. In the writings on Thermodynamics and the Theory of Available Energy, this lack of consecutive arrangement has remained until the present time a serious obstacle. In the notice\* of the first two volumes of the 'Collected Papers,' which was contributed to 'Nature' in 1885 by Helmholtz, the writer was so engrossed by this interesting episode as to devote nearly the whole review to its consideration; but even he has missed recognising that Thomson's "dissipation of energy" was in 1855 determined quantitatively just as much as Clausius' "entropy" was in the same month of the same year, and was, moreover, even then as wide in scope, making due allowance for the almost total absence

\* *Nature*, xxxii. (1885), pp. 25-7; Helmholtz's *Papers*, iii. p. 598.



of numerically exact physico-chemical data on which to develop it, as it had again become twenty years later in Helmholtz's own hands in 1882, or in those of Willard Gibbs in 1876-8.

Probably the severest ordeal to which a mass of occasional writings, evolving an entirely new range of thought, could be subjected, is that of republication after the lapse of years. The fragmentary character of the production of Thomson's papers, in scattered Journals and Transactions, naturally suggested ideas of obscurity to the workers who had time only to skim the contents of separate papers without absorbing them as a connected whole; but it will probably be granted to be a most remarkable circumstance, and irrefragable proof of sureness of construction in a subject so difficult and entangled, that the papers on Thermodynamics, which also founded the modern general Theory of Energy, were capable of being reprinted in full with but slight occasional erasures, and those mainly of unessential character. Here one is, of course, leaving out of account the preliminary struggle to reconcile the apparently conflicting principles of Carnot and Joule, which forms one of the most instructive and fascinating episodes in scientific history.

We may be permitted to surmise that it was in the keen insight of these early years that his mental habitudes became fixed. His most striking characteristic all through life was insatiable thirst for knowledge, unwearied inquiry and investigation at all times, in season and out of season, combined with sympathetic interest and charming deference and encouragement to any person, however junior, who was honestly bent on the same pursuits. It is not surprising that, with new and profound views breaking in upon him from all sides, it should have grown into settled permanent habit that no mode of occupation of his time was to be allowed to interfere with the claims of scientific investigation.

Already when he took his degree at Cambridge in the Mathematical Tripos in January 1845, it appears that many subjects closely connected with fundamental advances of the ensuing time were fermenting in his mind. It was only a few months afterwards that he at length, after years of search, discovered for the scientific world Green's 'Essay on Electricity' of 1828, ever since one of the classics of mathematical physics; he obtained, in fact by accident, a copy from his previous mathematical tutor, W. Hopkins, when he recognised how much of it he had anticipated by his own more intuitive results when still a boy. Soon afterwards he went to Paris to learn physical manipulation in the laboratory of Regnault—a fact which seems to have been forgotten when he recalled, in graceful terms, his obligations to the French science of his youth, in an address in connection with the celebration of the centenary of the Institute of France, of which the echoes vibrated through Paris. He has put on record that already even at that time, he went about among the Paris booksellers inquiring for a copy of another work of genius, which he was himself

to enroll among the few supreme classics of scientific knowledge, Sadi Carnot's small tract of 1824, 'Réflexions sur la Puissance Motrice du Feu'; he found in 1845 that it was quite forgotten, though they knew in the book-shops of the social and political writings of his brother Hippolyte Carnot, ultimately his editor and biographer (1878) in later years.

If one had to specify a single department of activity to justify Lord Kelvin's fame, it would probably be his work in connection with the establishment of the science of Energy, in the widest sense in which it is the most far-reaching construction of the last century in physical science. This doctrine has not only furnished a standard of industrial values which has enabled mechanical power in all its ramifications, however recondite its sources may be, to be measured with scientific precision as a commercial asset; it has also, in its other aspect of the continual dissipation of available energy, created the doctrine of inorganic evolution and changed our conceptions of the material universe. A sketch of the early history of this doctrine will illustrate the innate power and independence of Lord Kelvin's thought, as well as in some degree his relations to his great predecessors and contemporaries.

The initial difficulty of the subject lay in the feature, entirely novel to physical science, that in the inorganic world what we call dissipation or scattering of energy is loss only in a subjective sense; it concerns only the energy "available *to man*, for the production of mechanical effect," to use Thomson's own phrase of 1852.\* We can produce organised mechanical effect from diffuse energy such as heat, which consists in the unregulated motion of a crowd of jostling molecules, only by judicious guiding of its innate effort towards an equilibrium, just as we can get power from a turbulent waterfall by guiding the stream against a mill-wheel or turbine. But when the average of the molecular motions has come to a steady equilibrium throughout all parts of the material system, of which uniformity of temperature is the criterion, all chance of arranging or guiding part of its molecular energy into co-ordinated power available for our operations on finite bodies has passed away. This is, roughly, the *rational* of the principle of Carnot. Yet the energy has not disappeared: it is still there, but it is uniformly diffused and so not recoverable into the organised form of mechanical power. This absolute conservation of the total energy is the principle of Joule, which is the main experimental support of the presumption that all energy is ultimately of the dynamical type. In a complete view of physical transformations the two principles, of Carnot and of Joule, have both to find their places. Here a fundamental perplexity confronted and detained Lord Kelvin for some three years, 1847-50.

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\* Math. and Phys. Papers, i. p. 505.

When heat is allowed to flow away to a lower temperature without passing through an engine, its capacity for doing work has been dissipated. The opportunity for obtaining mechanical power from it has vanished beyond recall. Can then heat be correctly measurable as mechanical energy if some of the mechanical energy is lost irrecoverably every time that the heat diffuses to a lower temperature? Thomson, ever attracted by the engineering side of things, was dominated by Carnot's principle, as we have seen, even when as a youth in 1845 he went to Paris to Regnault's laboratory. Thus he at once set himself to explore its practical content by the aid of the mass of exact data on gases acquired by Regnault, as soon as these results appeared, in 1847, as the first instalment of the famous series of experimental researches, which had been subsidised by the French Government with a view to obtaining all the data that could be pertinent towards the improvement of knowledge of the principles of steam and gas engines. In Thomson's first paper towards this end, entitled 'On an Absolute Thermometric Scale founded on Carnot's Theory of the Motive Power of Heat, and calculated from Regnault's Observations,' he clears the ground for exact physical reasoning by elevating the idea of temperature from a mere featureless record of comparison of thermometers into a general principle of physical nature, making it a measure of the dynamical potentiality of heat, which is, on Carnot's principles, an intrinsic measure, i.e. quite independent of the substances in which the heat happens to be contained. But he cannot get rid of the impression that heat is something different from energy, which may produce energy in falling to a lower level of temperature, or on the other hand may diffuse passively so that this opportunity of creating energy is irrecoverably wasted. Such a view would tend towards the caloric theory which held that heat is somehow substantial; in terms of it Carnot, in fact, formulated his arguments. It has been remarked on this by Helmholtz that if Carnot had then possessed completer knowledge he would possibly never have hit upon his principle; on the other hand, his rough manuscripts, published many years after, have revealed that during the remaining six years of his short life he was inclining strongly towards the correct view on the nature of heat. In a footnote, Thomson gives expression to his own doubt. The experiments of "Mr. Joule, of Manchester," seem "to indicate an actual conversion of mechanical effect into caloric. No experiment, however, is adduced in which the converse operation is exhibited; but it must be confessed that as yet much is involved in mystery with reference to these fundamental questions of Natural Philosophy." And in a fuller account, soon after, of Carnot's Theory,\* as further developed numerically by aid of the data given by Regnault's experiments on steam, he adheres substantially to this position, "although this, and

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\* Trans. R. S. Edinburgh, January 2, 1849.

with it every other branch of the Theory of Heat, may ultimately require to be reconstructed upon another foundation when our experimental data are more complete." He returns, in a note, stimulated by a remark of Joule, to the problem of what becomes of the mechanical effect that appears to be lost when heat diffuses; but he cannot admit the suggestion of Joule to cut the knot by abandoning Carnot's principle, and he appeals to further experiment "either for a verification of Carnot's axiom, and an explanation of the difficulty we have been considering: or for an entirely new basis for the Theory of Heat." Still harassed by these doubts, he returns yet again to test the experimental verification of Carnot's principle (which he finds adequate) in an Appendix; \* for, as he says, "Nothing in the whole range of Natural Philosophy is more remarkable than the establishment of general laws by such a process of reasoning" as is that principle in its wider ramifications.

We have here found Thomson actually hesitating as to whether heat is to be classified as energy, on the ground that the fall of heat to a lower temperature can occur without developing any mechanical work. Yet it is true, as Lord Rayleigh has expressed it, † that most great authorities, especially in England, including Newton, Cavendish, Rumford, Young, Davy, etc., have always been in favour of the doctrine that heat is a mode of motion. The fact is, as we have seen, that Thomson knew too much to allow him to rest in such a partial view of things; he saw also a totally different side of the subject, which not even his close connection with Joule and appreciation of his work, could allow him merely to ignore.

Just a year before Thomson's first paper on Carnot's principle, Helmholtz, then a young army surgeon, had stepped (1847) into the first rank of physicists (though recognition came later, the memoir, e.g., becoming known to Thomson only in 1852) by the publication of the '*Erhaltung der Kraft*,' which asserted the universality of the conservation of total energy, and developed with convincing terseness and lucidity the ramifications of that principle throughout nature. To establish the transformation of heat into work he is already able to appeal to the classical experiments of Joule, published three years previously (1844)—not yet mentioned by Thomson, whether it was from want of knowledge or from some fancied mode of evading their force in the light of his insistence on Carnot's principle. These experiments proved definitely that expansion of a gas working against the pressure of the atmosphere absorbs an equivalent of heat, whereas expansion into a vacuum absorbs none. It was, in fact, in this paper that Joule rather summarily condemned Carnot's principle as above mentioned, on account of its supposed discrepancy with his own established results. And Helmholtz had naturally to consider this

\* April 30, 1849.

† The Scientific Work of Tyndall, Roy. Inst. Proc., Vol. xiv. p. 218.

point. He seems to have had access then only to Clapeyron's account of Carnot, of date 1843, from which, however, he expounds the argument succinctly and correctly. He admits the probability of the truth of Clapeyron's deductions for gases, but falls back on the suggestion that they may also be obtainable otherwise on more certain principles; while he characterises as very unlikely the (correct) inference that compression of water between its point of maximum density and the freezing-point would absorb heat. Thus Helmholtz,\* contrary to Thomson, saves the conservation of total energy by abandoning and ignoring the ideas belonging to the principle of Carnot.

The brilliant and suggestive writings of J. R. Mayer on the conservation of total energy were at that time unknown to Helmholtz: they seem to have been first brought to general notice† by Joule himself in the classical memoir on the Mechanical Equivalent of Heat presented by Faraday to the Royal Society in 1849. The sketch above given will have shown how little such theoretical considerations as those of Mayer, however illuminating and acute within their own range, were calculated to remove the profounder perplexities of Thomson, so long as there remained the apparently essential contradiction on which these doubts had their foundation. His insistence in class lectures on the absolute necessity for Joule's experimental work is still recalled by his students.

The credit of being the first to resolve these difficulties belongs to Clausius. In his memoir 'On the Motive Power of Heat and the Laws of Heat which may be deduced therefrom,' communicated to the Berlin Academy in February 1850, he quotes the title of Carnot's tract (Paris, 1824) in a footnote at the beginning‡ of the paper, which proceeds as follows: "I have not been able to procure a copy of this work: I know it solely through the writings of Clapeyron and Thomson, from which latter are taken the passages hereafter cited." Then, in the introductory section, after referring to the difficulties above discussed, and the work of Holtzmann, Mayer and Joule, he continues:—

"The difference between the two ways of regarding the subject has been seized with much greater clearness by W. Thomson, who has applied the recent investigations of Regnault, on the tension and latent heat of steam, to the completing of the memoir of Carnot.§ Thomson mentions distinctly the obstacles which lie in the way of an unconditional acceptance of Carnot's theory, referring particularly to the investigations of Joule, and dwelling on one principal objection to which the theory is liable. If it be even granted that the produc-

\* *Wissenschaftliche Abhandlungen*, i. p. 38.

† Osborne Reynolds, *Life of J. P. Joule* (Manchester Memoirs, vi.), p. 133.

‡ The quotations are here printed from Hirst's translation, in which this memoir occupies pp. 14-68.

§ *Trans. R. S. Edinburgh*, xvi.

tion of work, where the body in action remains in the same state after the production as before, is in all cases accompanied by a transmission of heat from a warm body to a cold one, it does not follow that by every such transmission work is produced, for the heat may be carried over by simple conduction; and in all such cases, if the transmission alone were the true equivalent of the work performed, an absolute loss of mechanical force must take place in nature, which is hardly conceivable. Notwithstanding this, however, he arrives at the conclusion that in the present state of science the principle assumed by Carnot is the most probable foundation for an investigation on the moving force of heat. He says: 'If we forsake this principle, we stumble immediately on innumerable other difficulties, which, without further experimental investigations, and an entirely new erection of the theory of heat, are altogether insurmountable.'

"I believe, nevertheless, that we ought not to suffer ourselves to be daunted by these difficulties; but that, on the contrary, we must look steadfastly into this theory which calls heat a motion, as in this way alone can we arrive at the means of establishing it or refuting it. Besides this, I do not imagine that the difficulties are so great as Thomson considers them to be; for although a certain alteration in our way of regarding the subject is necessary, still I find that this is in no case contradicted by *proved facts*. It is not even requisite to cast the theory of Carnot overboard; a thing difficult to be resolved upon, inasmuch as experience to a certain extent has shown a surprising coincidence therewith. On a nearer view of the case, we find that the new theory is opposed, not to the real fundamental principle of Carnot but to the addition 'no heat is lost'; for it is quite possible that in the production of work both may take place at the same time; a certain portion of heat may be consumed, and a further portion transmitted from a warm body to a cold one; and both portions may stand in a certain definite relation to the quantity of work produced. This will be made plainer as we proceed; and it will be moreover shown that the inferences to be drawn from both assumptions may not only exist together, but that they mutually support each other."

This memoir, as Willard Gibbs justly claims in his obituary notice (1889) of Clausius, laid securely the foundations of modern thermodynamics. But it seems equally true that this high merit lies mainly in the single remark at the end of the passage just quoted, which resolved the difficulties that had stopped Thomson; after that the development, though luminously accomplished, would have been plain sailing to any first-class intellect. Thomson's great memoir 'On the Dynamical Theory of Heat,'\* in which he at once connects Clausius' name with that of Carnot, appeared the following year. After giving a demonstration of the principle of "Carnot and Clausius" (§ 13), he proceeds (§ 14) to say that, about a year before,

\* Trans. R. S. Edinburgh, March 1851.

he had adopted this principle in connection with Joule's principle, notwithstanding that he could not then resolve the apparent discrepancy, as the basis of a practical investigation of the motive power of heat in air and steam engines. "It was not until the commencement of the present year that I found the demonstration given above. . . . It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius, who published his demonstration of it in the month of May last year, in the second part of his paper on the motive power of heat. I may be allowed to add that I have given the demonstration exactly as it occurred to me before I knew that Clausius had either enunciated or demonstrated the proposition. . . . The reasoning in each demonstration is strictly analogous to that which Carnot originally gave."

Once Thomson gets thus under weigh, as we have seen, by his own unaided efforts though anticipated by Clausius, he develops rapidly the thermal aspects of the subject, concurrently with Clausius and Rankine, but with wider generality, in particular avoiding their hypotheses connected with perfect gases. So little was he prepared to trust to a permanent gas thermometer as giving practically the intrinsic dynamical scale of temperature, that the following year he had already begun with Joule their series of laborious joint experiments to determine exactly how much the gas thermometer differs from the absolute scale. Their procedure was to deduce the result sought from observation of the slight cooling or heating produced by driving the gas under high pressure through a porous partition; with a perfect gas the process would be isothermal. When we consider that the results were to lead straight into the very core of molecular dynamics, the investigation may well rank to this day as one of the most striking advances in the record of physical science. It is noteworthy that Thomson in his own work kept on with the symbol for the unknown Carnot's function, until the dynamical scale had thus been experimentally investigated; though a gas thermometer was doubtless adequate to give to Clausius and Rankine indications of absolute temperature, so far as required for their preliminary approximate investigations over limited range. We have only to think of the modern physical undertakings steadily pushed downward toward the absolute zero of temperature, to realise that, except on the basis of Thomson's dynamical scale of 1847 and his method conjointly with Joule of exactly realising it in 1852, there could be no such thing as temperature in a scientific sense, and low temperature research would be devoid of most of its significance. These essential foundations for the scientific treatment of Energy were laid firmly in 1852, in a way that has held good without substantial modification ever since.

Perhaps this point, the rigorous scientific generality of the foundations on which he built from the beginning, could not be enforced

more strongly than by recalling that it is just this Thomson-Joule intrinsic cooling effect of expansion without external work, very slight under ordinary conditions, due merely to mutual separation of the molecules of the gas, that is the essential feature in the modern continuous processes for liquefaction of even the most refractory gases, by the expenditure of mechanical power to abstract the heat, which have now become familiar. On the other hand, the great economy of the reversed Carnot gas-cycle for ordinary refrigeration was pointed out in 1852, and applied by his brother to the ventilation of Belfast College.

In their parallel developments of the subject, while Clausius kept mainly to the theory of heat engines, applications over the whole domain of physical science crowded on Thomson. Already in December 1851 he communicates to the Royal Society of Edinburgh his Theory of Thermo-electric Phenomena, including the classical prediction of the convection of heat by the electric current, the so-called Thomson effect, which in the theory of electrons has a literal title to its original name. The formulæ of the printed abstract\* of this paper show that he must have been already in full command (December 1851) of Carnot's principle in its most generalised form—viz., as he expressed it in May 1854, but there introducing absolute temperature  $T$ , then recently determined by himself and Joule—that in a complete reversible cycle of change  $\Sigma (H/T)$  vanishes, or in differential notation  $\oint (dH/T) = 0$ , a form which was independently given by Clausius in December 1854, and from which the transition to Clausius' entropy-function (1856) is but a step. These advances appeared in full in the memoir, 'Trans. R. S. Edin.,' 1854,† where, in the way customary with him, he passes on to a long digression on the thermo-electrics of crystalline matter, including, after Stokes, the full theory of rotational vector effects. This latter subject was brought again into prominence many years after, when times were riper for it, with reference back to the present exposition, on the announcement by E. H. Hall of the discovery of an influence of this kind in electric conduction in a powerful magnetic field. Here also shines forth in a notable example what was always a main feature of Thomson's theoretical activity, the utilisation to the utmost of models and images of physical phenomena. He absolutely refused to deny to matter, however continuous and uniform as to sense it might appear to be, the possession of any property which he could imitate in a lattice structure or other architectural model, however complex; clearly, in his view, one has no right to assign limits *a priori* to the possible physical complexity of molecular aggregation.

One type of such limits, indeed, the only ones *a priori*, he vindicated in one of his most refined theoretical advances, those, namely,

\* Math. and Phys. Papers, i. pp. 316–323.

† Loc. cit., pp. 232–261.



which are imposed on reversible phenomena by the principle of the conservation of energy. The demonstration on these lines that there can be no rotational quality in either magnetic or dielectric excitation in continuous media afterwards became, in Maxwell's hands, one of the main confirmations in the general electric interpretation of optics, by leading at once to the validity of Fresnel's theory of double refraction.

But we must return from this digression. The cosmical aspect of Carnot's principle, in its reconciliation with that of Joule, had immediately arrested Thomson's attention, and the fundamental law of Dissipation of Energy in natural phenomena stood revealed in a brief note in April 1852, embodying the following momentous and carefully formulated conclusions :—\*

"1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.

"2. Any *restoration* of mechanical energy, without more than an equivalent dissipation, is impossible in inanimate material processes, and is probably never effected by means of organised matter, either endowed with vegetable life or subject to the will of an animated creature.

"3. Within a finite period of time past, the Earth must have been, and within a finite period of time to come the Earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be, performed, which are impossible under the laws to which the known operations going on at present in the material world are subject."

It is of interest to contrast this principle of degradation, or diffusion, of energy towards a uniform equilibrium, with the other great principle, dominating the phenomena of the organic world, which took shape at about the same time. Just fifty years ago biological thought was startled with the idea of the gradual evolution of organic forms, by the persistence, through hereditary transmission, of such accidental modifications as are adapted to the surrounding conditions of life, to the existing environment. In inorganic phenomena the energy becomes distributed among merely passive molecules; in the organic world the unit of investigation is an organism which has apparently the active property of fixing and transmitting in its descendants any structural peculiarity that it may come by. But even here there is something in common; the automatic evolution towards improved adaptation, in this case with no limit or equilibrium yet in sight, is attained at the cost of compensating dissipation, namely, the destruction of the individuals that happen to be ill adapted even though in other respects superior.

We observe in passing that in Thomson's formulation, Clause 2 already implies Clausius' conception (1854) of compensating trans-

\* Loc. cit., p. 514.

formations. What is perhaps now more interesting is that it expresses a decided opinion (which he still retained in 1892) on a question which Helmholtz \* to the end preferred to leave open, namely, whether the refinements of minute structure and adaptation in vital organisms may permit departure from the law of dissipation, which is known to be inflexible in the inorganic world, by utilising to some extent diffuse thermal energy for the production of vital mechanical power. The development of Clause 3 led to the famous series of investigations and discussions regarding the beginnings and the ultimate fate of our universe, and the duration of geological time, which have formed a region of intimate contact, but not always of agreement, between dynamical and evolutionary science.

Earlier in the same note, and also more fully in 'Phil. Mag.,' February 1853, Thomson illustrated his early complete grasp of all matters relating to the availability of thermal energy and to compensating transformations, in calculating the dissipation which arises from throttling steam, and the work which can theoretically be gained from the thermal energy in an unequally heated space.

This history is, however, not yet complete. Examination of the 'Notes inédites' of Sadi Carnot, appended to the reprint of the 'Réflexions,' published with charming biographical detail by his brother in 1878, and welcomed enthusiastically by Lord Kelvin, leaves an impression that Carnot was already struggling with difficulties of the kind to which the insight of Thomson exposed him some twenty years later. He had analysed (p. 91), with sure instinct, the Gay-Lussac experiment concerning heat of expansion of gas by efflux, and afterwards developed it (p. 96) into a suggestion of the identical porous plug experiment of Joule and Thomson. He points out (p. 92) that the view that heat is "*le résultat d'un mouvement vibratoire des molécules*" conforms to our knowledge in a long list of the principal transformations of energy; "*mais il serait difficile de dire pourquoi, dans le développement de la puissance motrice par la chaleur, un corps froid est nécessaire, pourquoi, en consommant la chaleur d'un corps échauffé, on ne peut pas produire du mouvement.*" He seems to be trying (p. 94) to think out a definite distinction between this movement of the particles of bodies and the "*puissance motrice*" into which it cannot be changed back. "*Si les molécules des corps ne sont jamais en contact intime les unes avec les autres, quelles que soient les forces qui les séparent ou les attirent, il ne peut jamais y avoir ni production, ni perte, de puissance motrice dans la nature. Alors le rétablissement d'équilibre immédiat du calorique et son rétablissement avec production de puissance motrice seraient essentiellement différents l'un et l'autre.*" "*La chaleur n'est autre chose que la puissance motrice, ou plutôt que le mouvement qui a changé de*

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\* See an interesting passage in his *Lectures on Heat*, posthumously published.

forme. C'est un mouvement dans les particules des corps. Partout où il y a destruction de puissance motrice, il y a en même temps, production de chaleur," and reciprocally. Like Thomson at the later date, he intended to seek the guidance of further experiment, outlines of which he sketched. These extracts suggest the very problems which are still fundamental in the molecular theory of Energetics, about which much is yet to be learned, though Thomson's theory of dissipation of energy and its molecular interpretation by Maxwell and Thomson and Boltzmann has illuminated the whole field. Yet Carnot already saw (p. 93) that his negation of perpetual motion demands that when heat does work in falling to a lower temperature, if some heat is really absorbed in the process the amount so absorbed must be independent of the mechanism of the process, must, in fact, be an equivalent of the work; for if the other alternative were possible, "on pourrait créer de la puissance motrice sans consommation de combustible et par simple destruction de la chaleur des corps." Clausius and Thomson had nothing in 1850 to add to this reasoning of date earlier than 1832.

No apology is required for thus dwelling at length on this episode in the evolution of the principles of physical science, the development of the principle of energy into its wider aspect, in which it assumes its universal co-ordinating rôle as the principle of available energy—involving its complete available conversation only in the limited class of phenomena that satisfy the Carnot test of being reversible, and in other cases emphasising the partial dissipation into diffused unavailable molecular energy which is characteristic of the operations of physical nature. No passage in the history of modern physics can, perhaps, compare with it in interest. In the other outstanding advance of the last century, the unravelment of the function of the æther as the sole means of intercommunication between the molecules of matter so as to constitute a *cosmos*, as the seat of the activities of radiation and of electric and chemical change, the problem to be solved was of a different type. The questions have there been more precise; they have suggested, and their investigation has been directed by, definite adaptable trains of experiment. But the pioneers in the theory of available energy had to probe among the *arcana* of common experience, in a manner which takes us back to the beginnings of dynamical science and recalls the efforts of Archimedes and Galileo and Pascal in detecting controlling principles in the maze of everyday phenomena.

The original stimulus to all this wide grasp of the relations of inanimate nature had its origin in the progress of mechanical invention, in the successful construction and operation of thermal engines. Irrespective of the problem of their industrial improvement, the detection of the essential features of this mechanical value of heat would appeal strongly to an analytical mind like that of Carnot. But his compact informing principle, as its content was ultimately developed in Thomson's hands, far transcended the special thermal problem from

which it started; it now dominates the whole range of physical science. It is only on its validity that our confidence is based, that we can treat the interactions of the finite bodies of our experience by strict mathematical and dynamical reasoning, entirely leaving aside, as self-balanced and inoperative, those erratic though statistically regular motions of the molecules, forming a very considerable part of the total energy, which constitute heat in equilibrium.

This fundamental basis of our knowledge of inanimate nature, thus acquired from clues suggested by human industrial improvements, still retains an aspect essentially anthropomorphic; it is conditioned by the limitations of our outlook as determined by the coarseness of our senses, as Maxwell seems to have been the first definitely to perceive. For the case of an ultra-material sentient creature of bodily size so small as to be comparable with a single chemical atom, his own sensible physical universe would be controlled by some fundamental law possibly of quite different type, while the phenomena which are prominent to us would take on for him a cosmical character as regards both time and space. We can ourselves catch partial glimpses of such a transformed physical universe, not subject to ordinary laws of matter in bulk, in the phenomena of high vacua, where the gaseous molecules come nearly individually before our attention and can almost be counted, and in the recent cognate phenomena of radio-activity either spontaneous or electrically excited. The boundary of demarcation of this new world from the universe which is dominated by the principle of available energy is naturally ill-defined: its exploration sheds light on both, and is perhaps the most interesting of the present activities of theoretical and practical physics.

Here also Lord Kelvin has played a part. Already in 1852, he had prefixed to one of his papers the title 'On the Sources available to Man for the Production of Mechanical Effect,' as if in anticipation of this anthropomorphic side of the subject, first broached apparently by Maxwell in 1871 at the end of his "Theory of Heat," where he points out that it is only man's inability to obstruct passively the individual molecules at will that prevents the whole of their energy from being available, and shows how sentient agents capable of doing this could reverse the otherwise irrevocable course of diffusion of the energy in a gaseous medium.

Perhaps Thomson's own most systematic pronouncement on the inner significance of these relations is a short paper in 'Proc. R. S. Edin.,'\* of date February 1874. He points out that the changes contemplated in abstract dynamics are strictly reversible; while in actual physical phenomena the absence of reversibility is conspicuous, a fact which was already embedded in the principle of dissipation of energy in 1852. Now "the essence of Joule's discovery that heat is diffused energy is the subjection of physical phenomena to dynamical law."

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\* Also *Nature*, ix. 1874, pp. 421-424; *Phil. Mag.*, March 1892, pp. 291-299.

Yet if we could reverse all inanimate motion, inorganic nature would unwind again its previous evolution; and if the materialistic hypothesis of life were true, living creatures could grow backwards with conscious knowledge of the future but no memory of the past, and would again become unborn. But the real phenomena of life infinitely transcend human science, and speculation regarding consequences of their ultimate reversal is utterly unprofitable. Far otherwise, however, is it in respect to the reversal of the motions of matter uninfluenced by life, a very elementary consideration of which leads to the full explanation of this theory of dissipation of energy." \* He then follows up the matter by illustrative applications of the theory of probability of a kind that in more recent times has led to a statistical definition of entropy rich in promise for applications to chemistry and to natural radiation.

The very interesting subject of the thermodynamics of radiation is only about twenty years old. Resting as it does fundamentally on the link with mechanical energy which is afforded by Maxwell's working pressure of radiation, Lord Kelvin would never admit its validity. The reason seems to be that he was never able to satisfy himself about any mechanical model of the relation of the atom to the æther that would give a mechanism for this pressural interaction between them. There are those who hold that the physical idea of an electron is sufficiently precise to make the *rationale* of light-pressure logical and secure. But Lord Kelvin would not consider it until he could visualise the whole process—see it in operation, as he used to say—to effect which completely would possibly go deeper than we may ever hope to penetrate; and this inability cut him off from what some consider to be the most refined and beautiful special development of the science which he founded.

The question naturally arises whether the establishment of the mathematical function that is fundamental for the theory of mechanical energy is not a subtler matter than this mere estimation of chances: in other modes of its investigation a powerful array of the dynamical properties of the medium is introduced. What becomes of them in the present aspect? The answer is, that the chance cannot be estimated aright until we know all the conditions, dynamical and other, to which the distribution of molecules is subjected. The dynamical relations find their place as conditions restricting the possibilities of random distribution. If through ignorance some of them are overlooked, the chances will be in error; each new condition that is discovered modifies to some extent the whole process, and thus amends our knowledge.

But this aspect of entropy is quite in keeping with the subjective character, so to speak, of available energy. Objectively, the dissipa-

\* Cf. Helmholtz's review already quoted, *Nature*, xxxii., 1886, *Wiss. Abhandlungen*, iii. p. 594.

tion of energy is merely the progress towards an equilibrium. As regards the purposes of man, whole regions of available energy may exist, of which he is ignorant, because he does not happen to have learned how to use them. The amount of energy available at a given temperature in a lump of carbon is possibly not yet exactly known: the process of turning it into heat before utilising it of course wastes most of it. Once, however, any slow reversible method of combustion has been discovered, in a voltaic battery for instance, the determination will be possible and may be effected once for all. Or, following a hint thrown out by Lord Rayleigh in 1875, afterwards developed more fully by Gibbs, we may make a rough estimate by applying the Carnot-Clausius formula to a cycle of which the upper temperature is that of spontaneous dissociation of the materials. We can, in fact, ascertain available energies only for systems which we can reach from a standard one by processes reversible in Carnot's sense.

Very early in Joule's investigations (1841) on the quantitative equivalence of various kinds of energy, he attacked the problem of the voltaic cell, and found his expectation verified, that in many cases the electromotive force was proportional to the thermal value of the chemical action of one Faraday equivalent of the reagent materials—provided he employed\* “galvanic arrangements adapted to allow the combinations to take place without any evolution of heat in their own localities.” He concluded that the condition thus laid down must be departed from in certain observed cases of discrepancy, and Thomson, in 1852,† conducted experiments to detect such local reversible heat. This principle of Joule was also stated quantitatively later, in a general way, by Helmholtz in the ‘*Erhaltung der Kraft*’ in 1847. It lies at the foundation of Thomson's memoir of December 1851, ‘*On the Mechanical Theory of Electrolysis*,’ whence the restriction above stated, the absence of local reversible heat, is quoted. *On this condition* the principle is exact; and the main point of Thomson's paper is the calculation, with a view to comparison with direct experiment, of the theoretical absolute value of the electromotive force of a Daniell's cell, from Joule's measurements of the heat developed by the combination of an electrochemical equivalent of its materials. The paper also developed the parallel between chemical energy and mechanical energy as sources of electromotive force, including the deduction by the principle of energy of the force induced by motion of a circuit across a permanent magnetic field. The further prosecution of the main subject, into cases where local reversible heat is developed (as evidenced by sensible change in electric conditions with

\* *Math. and Phys. Papers*, i. p. 477.

† *Loc. cit.*, p. 508; cf. also p. 496, where, in agreement with Joule, he ascribes the main loss to the work done by evolved gases in expanding against the atmospheric pressure.

temperature), remained for Gibbs and Helmholtz twenty-four years afterwards. In another paper of the same date, on absolute electric measurement, Thomson discusses Joule's thermal determination of absolute electric resistance of 1846, which afterwards proved to be more correct than the earlier values of the ohm.

Most interesting in connection with modern ideas is an abstract of February 5, 1852,\* again mainly expounding Joule's inspiring results and views on the transformations of energy. Thomson estimates from Liebig's data that about one-thousandth part of the total solar radiation incident on forest land is absorbed usefully by the trees, that being the amount recoverable as heat by their combustion. An intention to discuss these matters in connection with Carnot's principle, dealing also with the wave-lengths of the radiation, does not appear to have been fulfilled. Passing on to animal work, he estimates, after Joule, that as much as one-sixth of the energy of the food consumed can go directly into mechanical power. Then, relying on Carnot's principle, and Joule's discoveries regarding the heat of electrolysis and of electromagnetism, he proceeds to argue that "it is nearly certain that when an animal works against resisting forces, there is not a *conversion of heat into external mechanical effect*, but the full thermal equivalent of the chemical force is *never produced*—in other words, that the animal body does not act as a *thermodynamic engine*; and very probable that the chemical forces produce the external mechanical effects through electrical means."

Here he is emerging from the narrower theory of heat to the general theory of available energy, where heat is not the intermediary towards mechanical power; and we shall see presently how quickly he progressed in it. When it is recalled that at the time all this was going on, or immediately after, he was also laying the dynamical foundations of the phenomena of induced electric currents, including for example, the calculation of the period of the vibrations produced by electric discharges, the activity may well seem unprecedented; adequate exposition of the results had to fall behind.

The next stage (1855) in this series of investigations, the development of the ideas expressed in the extract just quoted, seems to demand special attention, for it is surely nothing less than the laying down of the precise laws of the all-embracing modern science of Free or Available Energy. The evolution of this generalisation can, as it happens, be traced. The memoir on 'A Mathematical Theory of Magnetism' has been already alluded to. In it, as everywhere else in Thomson's dynamical writings, the conservation of the potential energy, used there in the manner of Lagrange and Green and Mac-Cullagh and Helmholtz, in the sense of a potential of mechanical forces, is employed to determine the essential relations between

\* Loc. cit., p. 505.

physical properties. This use of the law of energy as a connecting principle afterwards became the note of Thomson and Tait's 'Treatise on Natural Philosophy.' In revising for press a continuation of this magnetic memoir, 'Phil. Mag.,' April 1855, where he is engaged in deducing magnetic reciprocal relations in more elementary fashion by use of a work-cycle, a thought occurred to him and was embodied in a footnote under date March 26, which will be quoted in full.\*

"It might be objected that perhaps the magnet, in the motion carried on as described, would absorb heat and convert it into mechanical effect, and therefore that there would be no absurdity in admitting the hypothesis of a continued development of energy. This objection, which has occurred to me since the present paper was written, is perfectly valid against the reason assigned in the text for rejecting that hypothesis; but the second law of the dynamical theory of heat (the principle discovered by Carnot and introduced by Clausius and myself into the dynamical theory, of which, after Joule's law, it completes the foundation) shows the true reason for rejecting it, and establishes the validity of the remainder of the reasoning in the text. In fact the only absurdity that would be involved in admitting the hypothesis that there is either more or less work spent in one part of the motion than lost in the other, would be the supposition that a thermodynamic engine could absorb heat from matter in its neighbourhood, and either convert it wholly into mechanical effect, or convert a part into mechanical effect and emit the remainder into a body at a higher temperature than that from which the supply is drawn. The investigation of a new branch of thermodynamics, which I intend shortly to communicate to the Royal Society of Edinburgh, shows that the magnet (if of magnetised steel) does really experience a cooling effect when its pole is carried from *A* to *B*, and would experience a heating effect if carried in the reverse direction. But the same investigation also shows that the magnet must absorb just as much heat to keep up its temperature during the motion of its pole *with* the force, along *AB*, as it must emit to keep from rising in temperature when its pole is carried *against* the force, along *DC*."

The exposition of the new branch of thermodynamics here referred to appeared in fact in the same month, April 1855, in the first part of the first volume of the 'Quarterly Journal of Mathematics,' under the title 'On the Thermoelastic and Thermomagnetic

\* Elec. and Mag., § 672. In a less definite way this principle had been effected already; cf. Mack, Principien der Wärmelehre hist.-krit. entwickelt. Early in 1849 James Thomson explains that it was his brother's pointing out to him that, on Carnot's principle, water could be frozen isothermally without requiring mechanical work, which set him on to the train of thought that predicted the lowering of the freezing-point by pressure and calculated its amount. As freezing is accompanied by expansion, a cycle involving freezing at a high pressure and melting at a low pressure, in fact confronted him with a perpetual motion, which he had to evade.



Properties of Matter, Part I.,' which represents the contents of the latter part of the paper to which the more general introductory matter was probably added. This paper was reprinted in 'Phil. Mag.,' January 1878, with some additional notes.\* The principles that we are now concerned with occupy the first few pages; the argument is expressed in terms of elastic strain, but that is obviously only for convenience of exposition. The total intrinsic energy  $e$  of a material system, measured from a standard initial configuration and temperature, is defined as a function of its actual configuration and temperature. It is established from Carnot's principle, as in the quotation above, that for transformations conducted entirely at the same definite temperature  $t$ , the mechanical forces applied to the system must be derivable from a work function  $w$  which represents, in fact, the potential energy acquired by the system in passing at that temperature from the standard configuration to the actual one. If  $\epsilon$  denote the simultaneous increment of  $e$ , then  $\epsilon - w$  must be the heat  $H$  taken in from outside during that change from the standard configuration, when conducted at the actual temperature.

It is to be observed that this simple consideration, which apparently here appears in science for the first time, carries the principle of potential energy in its mechanical application right back to Carnot's principle of 1824. In the previous writings on general potential energy, such as Helmholtz's 'Erhaltung der Kraft,' nothing of the kind is hinted at; while Clausius' treatment, being restricted to transformation of heat, is nowhere connected up with the general theory of energy. The first law of thermodynamics henceforth drops to more restricted scope, for it merely asserts that available energy when lost is changed into heat in equivalent amount. Yet it still suffices to maintain the presumption that all energy-processes have their source in—are consistent with—the ordinary Newtonian principles of dynamics as applied to ultimate molecules; considering the difficulty experienced by Thomson in reconciling Joule's law with his innate conviction of the validity of Carnot's principle, it is not surprising that this inference appealed to him with special force. Indeed, when the historical conflict between the two laws is kept in mind, the value of the first will not be disparaged. From this point of view the principle of Carnot appears in transformed aspect. Its chief interest is now transferred to the two creative ideas which it contains, the introduction into science (i) of the idea of a complete cycle of transformations, and (ii) of the criterion of absence of waste of power in any mechanical process, namely, that the process can be reversed, which includes the condition of temperature uniform throughout the system at each instant. The further development, including Carnot's function and the quantitative determination of the idea of temperature which it brings with it, is the thermal com-

\* Math. and Phys. Papers, i. pp. 291-316.

pletion of these fundamental principles of the general science of Energetics. When the illustrious originator of these ideas died in 1832 at the age of 86 he was in possession of the material to complete the train of essential principles himself.

Thus far we have secured a work-function  $w$  (available energy) for the applied forces at each temperature  $t$ , of form determinable by direct experiment. If such a function were known for every temperature, knowledge of the mechanical energy relations of the system would be complete. Thomson accordingly proceeds to connect these functions for adjacent temperatures by means of a Carnot cycle. In fact, he shows how to construct  $w$  as a function of both the configuration and the temperature, so that the same function shall, for each constant temperature, represent the energy then available for work.

The two functions, total energy  $e$  and work of available energy  $w$ , on which the complete science of Energy is thus founded, are naturally to be compared with the two functions, energy  $U$  and entropy  $S$ , which were made fundamental by Clausius in the very same month, April 1855—the tendency of the entropy of a *self-contained system* to increase being his mode of exact expression by Thomson's principle of dissipation. In fact, the distinction between the two methods is that Thomson's function  $w$  refers primarily to a system fed with heat so as to remain at constant temperature, while Clausius' function  $S$  refers primarily to an isolated system.

The principal operations of chemistry and physics are performed at constant temperature; thus it is Thomson's function  $w$  that is fundamental in the modern science of Energy, having been re-introduced by Willard Gibbs as "the characteristic function at constant temperature, and by Helmholtz as "free energy." The entropy is simpler to describe, and also to work with, except when the operations are isothermal; on the other hand, the "free energy" is a direct physical conception connecting up heat-energy in line with all other types of available physical energy, and thus transforming thermodynamics into the universal science of the relations of the statical transformations of Energy, namely, Energetics.

The function entropy seems to have been never employed in Lord Kelvin's investigations. As may be inferred from the above, it did not lie directly in his line of thought, which concerned itself with the physical entities energy and work. The idea of entropy is so directly suggested by his principle of dissipation, and the early mastery of the Carnot-Clausius equation  $\int (dH/T) = 0$  for a reversible cycle, in its widest form, which is shown in his theory of thermoelectric phenomena, that it could hardly have been strange to him; conceivably he never directly formulated it, because he had, in fact, developed a more directly physical scheme.

It is customary, after Thomson's own example, to call the relation

$\int(dH/T) = 0$ , as above, the Carnot-Clausius equation. It would provide the necessary complement to this nomenclature if his own equation between  $w$ ,  $e$ , and  $t$ , which is, in more usual notation, the equation of energy  $A$  available at constant temperature  $T$ ,

$$A = E + T \frac{\partial A}{\partial T},$$

and is now the fundamental principle in chemical physics through the far-reaching applications made by Gibbs, Helmholtz, van 't Hoff, Nernst, and other investigators, were known as the Thomson equation. His dominating position is indeed already widely, but not very definitely, recognised.

The question whether Thomson had prior knowledge of the entropy principle has been matter of some controversy between Clausius and Tait: on the view here taken it is relatively unimportant.

We may now recall in general terms the form of the principle developed into most varied applications by Willard Gibbs, with such power and invention as to constitute him the creator of a new science. The necessary increase of the entropy function  $S$  defines the trend of adiabatic transformation; the necessary decrease of the available energy function  $A$  defines the trend of isothermal transformation.

The two functions are immediately connected by noticing that the  $S$  in the given configuration exceeds  $S_0$ , that in the standard configuration at the same temperature  $T$ , by  $-\partial A/\partial T$ . We can render an isothermal transformation adiabatic by including in the system an infinite reservoir of heat at its own temperature, in the manner favoured by Planck: the change of total entropy is that of  $S - H/T$ , so that this function must always increase in an isothermal system. The reverse transition from adiabatic to isothermal would not be so direct. In fact, the entropy  $S$  is the convenient analytical function to employ when the temperature is different in different parts of the system, as is illustrated by the complexity of the calculation (already conducted in February 1853, in terms of Carnot's function  $\mu$ ) of the energy available for mechanical effect in such a system when self-contained,\* which is mainly of cosmical interest, and has probably drawn attention away from the principles of free energy, though the latter were again emphasised in Thomson and Tait's 'Natural Philosophy.'

This analysis of available energy by Thomson had not escaped the notice of Willard Gibbs (1876), though possibly only in its narrower connection with elasticity.† "Such a method is evidently preferable with regard to the directness with which the results are obtained. The method of this paper shows more distinctly the *role of energy* and

\* Thomson, loc. cit., p. 554. The calculation of the final uniform temperature is in fact based (p. 556) implicitly on constancy of the entropy.

† Scientific Papers of J. Willard Gibbs, i. p. 204.

*entropy* in the theory of equilibrium, and can be extended more naturally to those dynamical problems in which motions take place under the condition of constancy of entropy of the elements of a solid, . . . just as the other method can be more naturally extended to dynamical problems in which the temperature is constant." Gibbs then refers back to a previous note explaining the wider generality of his own method: its most salient feature is, however, the far wider development, by its author, into the doctrine of the chemical potentials of the constituent substances.

As throwing light on the stage at which scientific thought had arrived at the time Thomson was thus formulating the general science of Energetics, the following quotation from Helmholtz's important lecture,\* 'On the Interaction of Natural Forces'—delivered first at Königsberg, February 7, 1854, and in which he was the first to refer the replenishment of solar heat to gravitational shrinkage—is pertinent to our history. "These consequences of the law of Carnot are, of course, only valid provided that the law when sufficiently tested proves to be universally correct. In the meantime there is little prospect of the law being proved incorrect. At all events we must admire the sagacity of Thomson, who, in the letters of a long-known little mathematical formula which only speaks of the heat, volume and pressure of bodies, was able to discern consequences which threatened the universe, though certainly after an infinite period of time, with eternal death."

Later, in 1861, in writing of the constant surprises that arose in his work on acoustics, and the impression borne in upon him that new results develop themselves in the mind according to laws of their own, so that it seems to be hardly things essentially of his own invention that he is reporting, Helmholtz suggests that "Mr. Thomson must have found the same thing in his own work on the mechanical theory of heat."†

The end of this early period of pure scientific activity came when Thomson's enthusiastic encouragement of the costly practical enterprise of Atlantic submarine telegraphy entangled him in the solution of a whole class of practical problems, which only he could undertake, and which constituted one of the most strenuous tasks of his career. After the first cables had failed, in 1857-8, through wrong methods of working which entirely misconceived the situation, Thomson was given a free hand to make the most, under these expensive conditions, of the problem—in fact to get signals transmitted at profitable speed through a conductor, which, as he insisted, merely diffused electricity along it as heat travels along a bar, instead of conveying it, in compact pulses or waves. Here he succeeded by following out the pre-

\* English translation (by Tyndall), 1. 1873, p. 172.

† *Life*, p. 205.

visions of pure reasoning : for there could be little opportunity for making tentative experiments, according to the usual trial methods of inventors, such as, for instance, have so rapidly and brilliantly improved the arrangements for telegraphing across space, after Hertz had taken the preliminary crucial step of discovering, or rather recognising, the electric waves that are concerned in it. The necessities of this cable problem led largely to the invention of the fundamental principles of delicate and exact practical electrical measurement ; and though their embodiment in apparatus has naturally been subject to continuous improvement in detail, yet the principles remain largely those evolved in the early days by Thomson and his associates.

Among the most potent causes of the general improvement in physical modes of thought during the last third of the century, was the appearance, in 1867, of what then purported to be merely the first volume of the 'Treatise on Natural Philosophy,' by W. Thomson and P. G. Tait, which has proved to be a turning point in the exposition and expression of physical science, at any rate in this country. The preparation of this book, which had gone on for some years, induced frequent visits by Thomson to his friend and disciple Tait, at Edinburgh. Among other things, this treatise revised the terminology of dynamics, which had been allowed to grow up, in many respects, in forms that retained only historical meaning ; the impulse thus given, which had indeed already been operating less systematically in the previous years, and was largely due doubtless to his brother James Thomson, has led, in the hands of Maxwell, Heaviside and others elsewhere, to greater attention to the language of science, the introduction everywhere of expressive terms, which react powerfully in inducing clearness of ideas. Another of the benefits conferred by this work was that it served, in some degree, to focus the scattered fragments of Thomson's own investigations and those of his associates, and to exhibit his scientific method, as exemplified in the subjects covered in this first instalment, which contained general kinematics and dynamics, general theory of the potential, and theory of elasticity with extensive geodetic application.

A translation of this book into German, by Helmholtz and Wertheim, appeared in 1871-4. In a preface, Helmholtz pointed out how it satisfied, in very remarkable manner, a most urgent want in higher scientific literature. Previously there had been no resource but to go to original memoirs, difficult of access even if one knew where to find them ; and on this account the recent progress of connected mathematical physical thought had been halting. Moreover, as he said, when a worker like Sir William Thomson admits us to participate in the very upbuilding of his ideas, exhibits to us the modes of intuition, the guiding threads, which have helped him, by bold combinations of thought, to control and arrange his refractory

and entangled materials, the world owes him its highest gratitude. Helmholtz goes on to contrast the universal outlook of such a book, involving unavoidable lacunæ and difficult transitions, with the beautiful precision of the best special treatise of the earlier period. But the reader who does not spare himself the necessary effort towards mastery reaps an ample reward; he will find himself trained and equipped for the task of appreciating and extending knowledge, to a degree that he could never have attained from mere passive assimilation of sharply cut formal demonstrations. Valuable to the same end is the constant endeavour of such a work to employ those mathematical methods that keep close to actuality, are amenable to detailed interpretation: though they are naturally much harder, especially at first, than a strictly ordered analytical calculus would be, there remains the permanent gain of direct insight into the processes and relations of nature. Finally, allusion is made to difficulties encountered by the translators, arising from the originality of the treatment, and the series of new scientific terms that the authors had, in consequence, introduced.

This appreciation, by the most competent living master, set out justly the advantages and defects of Thomson's method of work. He never had time to prepare complete formal memoirs. It was but rarely that his expositions were calculated to satisfy a reader whose interests were mainly logical; though they were almost always adapted to stimulate the scientific discontent and the further inquiry of students trained towards fresh outlook on the complex problem of reality, rather than to logical refinement and precision in knowledge already ascertained. Each step gained was thus a stimulus to further effort. This fluent character, and want of definite focus, has been a great obstacle to the appreciation of "Thomson and Tait," as it is still to Maxwell's "Electricity," for such readers as ask for demonstration but find only suggestion and exploration. There is perhaps nothing that would contribute more at present to progress in physical thought than a reversion, partial at any rate, from the sharp limitation and rigour of some modern expositions to the healthy atmosphere of enticing vistas which usually pervades the work of the leaders in physical discovery. With increased attention to the inspired original sources of knowledge the functions of a teacher would be more than ever necessary, to point to the paths of progress and to contrast the effectiveness of different routes, as well as to restore valuable aspects which drop away in formal abstracts; science would thus adhere to the form of a body of improving doctrine rather than a collection of complete facts.

The establishment of significant terminology in dynamics was made still more effective by material illustration of the principles thus connoted. For example, the law of conservation of rotational momentum, of which the germ was already in the *Principia*, had been developed by d'Alembert and Laplace into complex formulæ which

were interpreted cumbrously in terms of the idea of description of areas, introduced long before by Kepler and Newton for the simple case of the motion of the planets. Building on the introduction by Poinso<sup>t</sup> of the idea of rotational effort or torque, Thomson set about making the rotational momentum possessed by a body an intuitive fact, like its mass or volume or density, instead of a mere complex mathematical expression. The subject was illustrated in his lectures by experiments intended to develop a direct sense of the elastic stiffness of balanced spinning masses. The gyroscope of Foucault, with its special gimbal suspension, became the gyrostat, in which the spinning body was enclosed and protected by a frame or box, and could thus be manipulated readily in many ways, e.g., either balancing itself on an edge, or on stilts, or being hung on to a pendulum with free suspension; it could thus assist towards realising varied knowledge of the properties conferred by this newly recognised type of permanent possession of matter—the intrinsic spin of a free body, which in the absence of friction of the bearings would be retained for ever—which has in fact more recently become a branch of experimental engineering.

This idea of spin, as a possible essential endowment of masses of matter, was constantly being extended in many directions. In particular it came to be the foundation of the first, and hitherto the only fairly successful, mechanical representation of the working of the æther of space. Though Thomson's early mathematical elucidations and demonstrations of Faraday's ideas formed a main part of the material which Maxwell welded into a connected theory of electricity, which afterwards extended itself into optics and general radiation, his own mode of investigation took on rather the reverse order. For he could imagine no direct mechanical model wide enough to include the various sensible modes of working of electricity, which he had himself elucidated in special domains from the doctrine of transformation of energy and the principles of Ampère and Faraday. Thus he turned aside to attack the more compact and definite problem of discovering the type of an æther that would satisfy merely vibratory requirements, those namely of light and radiation. Long-continued efforts to base its properties on elasticity arising simply from solidity, after the manner developed by Green, though evolving many fruitful aspects of elastic propagation in continuous physical media, had all ended in failure. Why not then try this elasticity of rotation instead of elasticity of form? The result was immediate success. But, as embodied in a model—only theoretical it is true, but one whose construction could be distinctly contemplated, and has since been in part made practically effective in the form of gyrostatic apparatus for steadying ships relatively to the vertical—the achievement carried wider consequences than this. It formed the objective justification of a purely analytical solution of the same problem which had been offered by MacCullagh, of Dublin, fifty

years before. That investigator had, in fact, shown that all the optical functions of the æther were 'consistent with Lagrange's abstract relations, in which the essential content of Newtonian dynamics had been concisely formulated free from the material accidents attaching to special systems and mechanisms. MacCullagh's abstract mathematical solution had, however, been widely repudiated, because it went beyond such conceptions as could properly belong to ordinary static material phenomena. But rotational momentum, as a possible endowment of matter, had been overlooked in this criticism : and Lord Kelvin's ideal model was thus the justification of MacCullagh's theory of light—which, once it became favourably appreciated, now extended itself most readily and naturally to include the whole field of electric phenomena, which appeared as non-vibratory modes of disturbance of the same æther—thus in fact exhibiting the Maxwellian theory developed in the reverse direction from optics to electrics.

All his life Lord Kelvin was keenly interested in such potentialities of intrinsic latent spinning masses, as a possible factor in the ultimate explanation of the sensible qualities of bodies. In ordinary physics, the elasticity of solids is merely taken as something existing, without attempt at explanation of its origin, but with full utilisation of the restrictions as to type which the principle of energy imposes. Hence the significance of the Royal Institution Lecture of 1881, with its copious and beautiful illustrations, entitled 'Elasticity viewed as possibly a Mode of Motion'—viewed in fact as possibly stiffness induced in matter, itself non-elastic, by latent intrinsic spin—and more fully developed in the British Association Address of 1884, 'Steps towards a Kinetic Theory of Matter.\*'

It has been recalled that the elastic properties of the æther can be imitated by a model composed of connected rotating masses, too complex, of course, to be actually made, but which can quite definitely be imagined. The fascinating question whether all physical action can thus be ascribed to latent phenomena of motion was always to the fore in Thomson's thought. The refined experimental proofs by Joule that mechanical energy never vanishes, but when apparently lost is still traceable as the diffuse energy of heat, afforded to him the strongest presumption that all manifestations of energy are subject to the principles of dynamics as resolved into their essential elements by Newton. This conviction would be the stronger, from the fact that for two years or more he was at a loss to reconcile Joule's principle with the doctrine of Carnot, which had very early obtained a firm hold on his mind. The reconciliation came through the distinction drawn between total energy and available energy; the deeper meaning of the principle of Carnot was simply (1874,

\* Popular Lectures and Addresses, i.



following Maxwell) that the mechanism of physical energy is so minute in scale of magnitude as to be only partially under the control of man. Is it possible to reduce all potential energy, electric or otherwise, to the ultimate simplest terms, as interactions of latent cyclic motions, such as he was constantly occupying himself with, in connection with his gyrostats?

At one period, from 1867 onward, Thomson made a very determined effort to carry a special scheme of this kind as far as it could go, in the form of the theory of vortex atoms, to which he devoted some of his most original and powerful efforts, building on the famous hydrodynamic theorems of Helmholtz which have exerted so great an influence in modern physical thought. To Lord Kelvin, at this time,\* prompted by a magnificent display of smoke rings recently witnessed in Tait's lecture room where they rebounded from one another as if made of rubber, the discoveries of Helmholtz inevitably suggested that vortex rings "are the only true atoms," as they evade the customary "monstrous assumption of infinitely strong and infinitely rigid pieces of matter," while they have permanent individuality and free periods of vibration, in that respect probably passing beyond any ideas present to the mind of Rankine, when in 1850 he treated of 'Molecular Vortices' in connection with thermodynamics. The vortex ring would also be "strong and durable," an unchanging element, in a way that a vibrating congeries of more elementary discrete ultimate atoms could not be.

We have also seen him engaged in the same task of illustration of elasticity and other properties of matter, by systems of rigid gyrostats connected by mechanism, in place of the flexible vortex rings affected only by the fluid medium in which they subsist. Thus, in 1856, he illustrated Faraday's magneto-optics by calculating the duplication of the period of oscillation of a pendulum, which is produced when a gyrostat is hung from it—a problem which, as Gray remarks, bears directly on the mode of explanation of the modern Zeeman effect, rather than of its converse the original magneto-optic influence of Faraday. The general treatment of these problems of latent steady motions, forming perhaps the most notable modern extension of physical dynamics, originated in the second edition of Thomson and Tait's 'Natural Philosophy,' published in 1879: the requisite analysis was, however, introduced in simpler and more compact form by Routh two years previously, in his essay on 'Stability of Motion,' where everything was expressed in terms of a modified Lagrangian function, described later by Helmholtz, whose writings expanded the theory in many directions, and made it more widely known, as the "kinetic potential."

The recreation of yachting, by which Thomson was wont to

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\* Phil. Mag., July 1867, pp. 15-24.

recruit his energies in summer, reacted naturally towards the improvement of nautical affairs. His dynamical instinct, and experience in the invention of delicate instruments, found a congenial field in placing the ship's compass on a scientific basis. The heavy cumbersome magnets, swinging on pivots under unsuitable conditions, were replaced by the well-known systems of needles, delicately suspended yet insensitive to shock, so small that the iron masses compensating for the magnetism of the ship could be effectively introduced in moderate size. Again, by the use of steel wire, he worked up the modern method of taking reliable soundings from a ship in motion, the depth being calculated from the compression of the air in a narrow glass tube attached to the sinker. But the most remarkable feat in this domain was the thorough practical mastery of the complicated phenomena of the tides, achieved mainly under his direction, and culminating in the invention, about 1876, of simple automatic mechanism for performing all the laborious calculations of tidal harmonic analysis, both direct and inverse. The tides are controlled by the Sun and Moon, and so repeat themselves very closely in periods of nineteen years. But there is another far more fundamental and instructive way of investigating them. To every periodic (simple harmonic) component in the motion of either Sun or Moon relative to the Earth, there corresponds a component of the same periodic time in the tide produced by them at any place, and there are no other components; yet to calculate their amounts directly with the existing irregular contours and depths of the ocean would be a problem practically impossible. The method of harmonic analysis, as first initiated in this subject on a much smaller scale by Laplace, allows us to deduce, from a tidal record for a sufficient length of time, the amplitudes and phases of these harmonic components of known periods; and when the more important ones have been thus determined, the prediction of future tides becomes a matter of merely summing up the harmonic constituents, no matter how complex the physical conditions at the place in question may be, so long as they are unchanging. All this and much more can now be done by the machines invented by Lord Kelvin and his brother,\* though, owing to the preliminary imperfection of construction of the analysing machine, it is at present found to be safer and not very troublesome to determine the amplitudes of the components by calculation. This achievement—the complete mastery of the tides by means most simple but adequate—is perhaps the greatest triumph of the method of Fourier, which has always been one of the advances most admired by Lord Kelvin in modern physical mathematics. After this success it was natural to apply the same method of harmonic analysis to meteorological phenomena, including the atmospheric electricity which he had investigated many years before, which also are con-

\* See Thomson and Tait's *Nat. Phil.*, ed. 2, Appendices.

trolled by Solar influence; but here the problem has proved not to be so feasible, the definite periodic components being so mixed up with the erratic results of meteorological instabilities that not much has yet come out of the effort.

In later years Helmholtz paid many holiday visits at Largs, and enjoyed the yachting expeditions, which provided a refuge for him from the attacks of hay fever. In 1871, the two friends studied the theory of waves which Thomson "loved to treat as a kind of race between us." It was shortly before that Thomson had broken new ground suggested by observations from his becalmed yacht, on the theory of capillary ripples, and on the waves produced by wind and current, treated in two letters to Tait intended for the Royal Society of Edinburgh. In later years the latter subject was discussed in much more detail and developed in new directions by Helmholtz, with a view to meteorological atmospheric applications.\*

On board the yacht, Helmholtz reports† that "It was all very friendly and unconstrained. Thomson presumed so much on his intimacy with them that he always carried his mathematical notebook about with him, and would begin to calculate in the midst of the company if anything occurred to him, which was treated with a certain awe by the party. How would it be, if I accustomed the Berliners to the same proceeding? . . ."

In 1884 Sir W. Thomson delivered the well-known course of lectures on 'Molecular Dynamics and the Wave Theory of Light,' at Johns Hopkins University, Baltimore, after attending the meeting of the British Association at Montreal. The papyrograph unrevised report, issued in December 1884, by Mr. A. S. Hathaway, may justly be said to have reawakened, or at any rate strongly intensified, interest in the ultimate form of the problem of æther and radiation, both in this country and abroad. It seems fair to say also that the interest and value of the lectures arose largely from the unpreparedness of their author. As his audience of American physicists fed him from day to day with the more recent experimental and theoretical results relating to selective absorption, which were largely new to him, they had before them the spectacle, on which Helmholtz had laid stress, of one of the great minds of the century struggling with fresh knowledge and trying to assimilate it into his scheme of physical explanation, calling up all his vivid store of imagery and analogy to aid. His auditors at the time, and his readers afterwards, thus must have considered the lacunæ and difficulties as their own personal problems in which they were assisting. Perhaps no exposition in physical science so vivid and tempting has ever been published; and for many years afterwards scientific activity in these subjects was strongly tinged by the Balti-

\* Cf. Baltimore Lectures, Appendix G, and Prof. Lamb's Hydrodynamics.

† Life, p. 287.

more lectures, which transformed optics for the time from an affair of abstract mathematical equations into a subject of direct physical contemplation, in close touch and analogy with the objective manifestations of ordinary dynamics.

In the preface to the authoritative edition of 1904, which in the twenty years' interval had grown to be a volume of some 700 pages octavo, Lord Kelvin in fact describes the object of the course of lectures as follows: "I chose as subject the Wave Theory of Light with the intention of accentuating its failures, rather than of setting forth to junior students the admirable success with which this beautiful theory had explained all that was known of light before the time of Fresnel and Thomas Young, and had produced floods of new knowledge, splendidly enriching the whole domain of physical science. My audience was to consist of professorial fellow-students in physical science; and from the beginning I felt that our meetings were to be conferences of coefficients\* in endeavours to advance science, rather than teachings of my comrades by myself. I spoke with absolute freedom, and had never the slightest fear of undermining their perfect faith in ether and its light-giving waves; by anything I could tell them of the imperfections of our mathematics; of the insufficiency or faultiness of our views regarding the dynamical qualities of ether; and of the overwhelmingly great difficulty of finding a field of action for ether among the atoms of ponderable matter. We all felt that difficulties were to be faced, and not to be evaded; were to be taken to heart, *with the hope of solving them if possible*; but, at all events, with the certain assurance that there is an explanation of every difficulty though we may never succeed in finding it."

He goes on to say that he had now, in 1904, virtually got to the bottom of the difficulties of 1884. He thinks, too, that in the wider field of æthereal phenomena *everything non-magnetic* can be explained "without going beyond the elastic solid theory," but *nothing magnetic*. "The so-called electro-magnetic theory of light has not helped us hitherto; but the grand object is fully before us of finding comprehensive dynamics of ether, electricity, and ponderable matter, which shall include electrostatic force, magnetostatic force, electro-magnetism, electro-chemistry, and the wave theory of light."

His purely scientific activity from 1884 onwards hinged largely on the production of the definitive edition of these lectures, which, in terms of the remarks just quoted, had raised up in front of him all the difficulties in modern optical and general æthereal theory. The resulting volume, with its numerous insertions, including most of pp. 280-468, and the twelve Appendices occupying pp. 648-700, may take rank in fact as virtually Volume IV. of the 'Mathematical and Physical Papers.' \* Among the vast array of new and recent material collected into the volume there may be mentioned the following:

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\* In the literal sense of the term.

theory and observation on the opacity of air and gases, reflexion from diamond and from metals, his various attempts at elastic solid vibratory theories of the æther, rotation of the plane of polarisation combined with double refraction, waves on water and in dispersive media with the residual disturbance they leave behind, waves raised by wind or by ships, the total mass of the material universe, various theories of electrons or electrions as he preferred to call them; also much regarding molecular tactic of crystals and the resulting dynamics, this time on a Boscovichian foundation. The Royal Institution lecture of 1900, on 'Nineteenth Century Clouds over the Dynamical Theory of Heat and Light,' is also included: these difficulties he there reduces to two: the difficulty regarding the motion of matter through æther, which he thinks is "not wholly dissipated," and the difficulty about the frittering away of the energy of gaseous molecules among their numerous periods of free vibration, which he solves in what may possibly be held to be the natural way, by denying the proofs.

Little has been said here with regard to Lord Kelvin's masterful and most effective preoccupation with the development of modern electric engineering, which has now almost completed the transition from the age of steam to the age of electric power. In this new branch of applied science, his active perception of the essentials of progress assumed the form of generalship; most of the details of progress naturally came from others, but he was ready always to emphasise the salient problems, and to acclaim, early and enthusiastically, such nascent inventions as would be pertinent to their mastery. An example is afforded by the emphasis with which he hailed the invention of the original Faure storage cell or accumulator,\* which promised to supply the improvements (including the subdivision of a large storage battery to play the part of a step-down transformer, not yet practically effective) then necessary for economical development of the electric generation of power. This subject came particularly to the front in his Presidential Address in 1881, at York, to the Physical Section at the Jubilee Meeting of the British Association, 'On the Sources of Energy in Nature available to Man for the Production of Mechanical Effect,' which almost repeats the title of his early paper of 1852, but is this time concerned with the practical utilisation of these sources, now rapidly ripening, whereas the earlier discussion related to their philosophical detection and estimation. In this Address, after referring to Siemens' suggestion, three years previously, of the electrical transmission at high potential of the power of Niagara Falls, itself resting, as he remarks, on Joule's early experimental discovery that in an electromagnetic engine as much as 90 per cent. of the energy of the driving current can be utilised, he proceeds to summarise his own conclusions regarding economy of trans-

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\* Brit. Assoc. Report, 1881, p. 526.

mission over long distances, as communicated in the form of evidence to a Parliamentary Committee two years before. The brief paper, now classical in electro-technics, then communicated,\* 'On the Economy of Metal in Conductors of Electricity,' is an early notable instance of the blending of economics with exact physics: the solution of the problem "would be found by comparing the annual interest of the money value of the copper with the money value of the energy lost annually in the heat generated in it by the electric current. The money value of a stated amount of energy had not yet begun to appear in the city price lists." He shows that the gauge to be chosen for the transmitting conductor does not depend on its length, but solely on the strength of the current to be employed. He was much concerned also in the early evolution of dynamos (the term had been introduced by him about this time as a contraction for dynamo-electric machine), the designing of which was to become entirely effective a few years later by means of the graphical methods introduced by Hopkinson. Perhaps the earliest domestic installation of electric lighting in this country was the experimental one which he established in his house at the University of Glasgow; while one of the early public installations was the one, still in operation, which he presented, in connection with the celebration of the six hundredth anniversary of the foundation of that most ancient house, to his College in Cambridge, which had been able, under new statutes, to re-elect him to the Fellowship that he had vacated long before on his marriage.

The introduction of heavy currents and voltages in engineering required the provision of suitable instruments of measurement. This was always a congenial task: his graded series of current-weighers or ampere-meters, and of volt-meters—embodying those theoretical principles of adequate support free from constraint or strain, in mechanical design, on which he always insisted, to the great improvement of general practice in such matters—have proved to be of fundamental service wherever exact measurement is essential.

His interests ramified into all departments of human activity: even his physical writings were often relieved by play of allusion to literature and history. In his later years he took an active and zealous part in political affairs, and attended regularly the sittings of the House of Lords. In his undergraduate days he was one of the founders of the Cambridge University Musical Society, playing the French horn at its opening concerts in 1843, and becoming president in due course. Later he published some observations † on the beats of imperfect harmonies of simple tones, tending to a conclusion different from that of Helmholtz which referred the beats to combination tones.

All this activity implied a robust constitution. As an undergraduate at Cambridge, he found time to take a keen interest in

\* Brit. Assoc. Report, 1881, pp. 526-8.

† Roy. Soc. Edin. Proc., 1878.

manly sports, rowing in the Peterhouse boat, which had second place on the river, and winning the Colquhoun sculls, then, as now, one of the main objects of athletic ambition. Afterwards he was expert at curling, until a serious accident on the ice stopped the pursuit and left him slightly lame for life. His subsequent yachting and cable-laying experiences have been already referred to.

The general impression produced, at first sight, by the four volumes containing the collected scientific papers up to 1860, might well be a somewhat vague notion of desultory, though profound, occupation with the ideas that were afterwards to be welded by more systematic expositors into our modern theoretical knowledge of mechanical and electrical and optical philosophy. At first glance, the exposition in characteristically practical terminology might even suggest that these papers were concerned with the engineering achievements by which he is most widely known, as much as with new theoretical foundations for physical science. Closer attention has compelled the conclusion that the results of his activity in the early period from 1845 to 1856 are perhaps unique in modern scientific annals; at any rate there can have been few parallels since Newton and Huygens and their great predecessors. It is said that Lagrange qualified his profound admiration for the genius of Newton by the reflection that only once could it be given to a mortal to have a system of the stars to unravel. Somewhat in the same way one might imagine the reflection of a seer of the future, that it can hardly be given again to a man of genius to have, in his first dozen years of creative intellectual activity, the ideas and discoveries of a Carnot, a Faraday, and a Joule, to interpret and develop for mankind.

His only peer in general physics in those early days, as also later if we exclude his own disciples, was perhaps Helmholtz. They began their careers of investigation about the same time, but at first their paths did not lie much together. For in his early years Helmholtz's professional work was that of a physiologist, though in the essay on the 'Conservation of Energy' he revealed, in 1847, his true bent as a leader in the exploration of the underlying principles connecting the different departments of the fundamental science, general physics. By the time this famous essay came into Thomson's hands, in 1852, he had himself travelled, with Joule's assistance, as far as it reached, if we except some special applications; but much more, he had in fact already dug down, on the inspiration derived from Carnot, far into the true foundations of the doctrine of Energy as available and recognisable to man, evolving from it ideas now familiar, but then of revolutionary significance, as regards both dynamical science and cosmic evolution, of which no one up to that time had any definite notion. The saving virtue of physical or any other genuine science is, that the most essential discoveries of one generation become worked up so as to be obvious and almost axiomatic to the next. The charm

of the study of scientific history is thus to trace the beginnings of creative ideas, to see how slight sometimes was the obstacle that delayed the discovery of a new field of knowledge ; though here the temptation to read back our own refined knowledge into the past lays many snares. In no part of science is this interest greater than in the doctrine of Available Energy ; the generality of outlook, leading to recasting of the fundamental ideas regarding physical force and power, which was secured by Thomson away back in the fifties, is on the least favourable view a matter for wonder.

In the years following, the powers of Helmholtz were concentrated largely on his great task of the exploration of the physical foundations of the activity of the senses, a subject of fundamental importance because they supply our only outlook into the external world ; while Thomson's efforts were employed in the problem, then urgent and preparatory to Maxwell, of the dynamical interpretation of the ideas of Faraday, and in the creation of the fundamental science above referred to which constitutes Thermodynamics in its widest sense, the all-pervading doctrine of Available Physical Energy to which it seems appropriate that Rankine's name Energetics should belong. In later days of close friendship their fields of activity had much in common, Helmholtz apparently often brooding over, and developing into fuller and more varied aspects, fertile points of view, such as the influence of wind and surface-tension on waves, and the generalisation of dynamics by the inclusion of latent cyclic motions, that had been already thrown off in more summary fashion by his colleague. On the institution of the Helmholtz memorial medal, the first award was to Lord Kelvin.

In a letter to Tait in 1876,\* who was preparing a biographical notice for 'Nature,' Helmholtz had given an estimate of the work of his friend at that period. "His peculiar merit, according to my own opinion, consists in his method of treating problems of mathematical physics. He has striven with great consistency to purify the mathematical theory from hypothetical assumptions that were not a pure expression of the facts. In this way he has done very much to destroy the old unnatural separation between experimental and mathematical physics, and to reduce the latter to a precise and pure expression of the laws of phenomena. He is an eminent mathematician, but the gift to translate real facts into mathematical equations, and *vice versa*, is by far more rare than that to find the solution of a given mathematical problem, and in this direction Sir William Thomson is most eminent and original. His electrical instruments and methods of observation, by which he has rendered, amongst other things, electrostatical phenomena as precisely measurable as magnetic or galvanic forces, give the most striking illustration how much can be gained for practical purposes by a clear insight into theoretical questions ;" and the series of his papers on thermodynamics



and the experimental confirmations of several most surprising conclusions deduced from Carnot's axiom, point in the same direction."

We have seen the hints and principles thrown out by Thomson in such profusion fructify in patient development by other great investigators, so that it would be difficult to name a branch of modern physical science in which his activity has not been fundamental. In one phase of his thought it becomes cosmical, and transcends experimental aids. All through life his ideas were wont to range over the immensities of the material universe, reaching back to its origin and onward to its ultimate fate. In his youth he established the cardinal principle of inanimate cosmic evolution, as effected through the degradation of energy, which determines the fate of worlds, and is the complement of the principle of evolution in organic life which came to light at about the same time. In another aspect of this principle, asserting that the trend of available energy must always be downwards, it has developed into the key to the course and the equilibrium of voltaic and chemical change, and to all other branches of physical knowledge in which the atomic nature of matter is the pervading influence. The greatness of the revolution thus effected in physical science, and in its industrial applications which are in strict relation to this available energy, requires no emphasis. The magnitude of the advance brought by the mere enunciation of the principle of dissipation is to be measured by the very inevitableness of this law to our present modes of thought; it is difficult now to recognise the limitations that must have belonged to the time when its formulation caused such surprise and wonder.

At the end of his strenuous career his thoughts reverted again to these problems of the origin and destiny of material things. Novel considerations were brought to bear, with intellectual vigour appropriate to youth, to demonstrate even the finiteness of the material universe—such, for example, as the darkness of the firmament and the moderate magnitude of the relative velocities of the most distant stars. In the last weeks, he pondered over the remote history of our own planet, and reasoned with striking force and lucidity, as may be read in a posthumous paper, on the antiquity of its continents and oceans, reaching back possibly to the time when the Moon separated from the Earth.

In this sketch the chief aim has been to set out a connected historical view of the course of Lord Kelvin's scientific activity and its relation to his contemporaries. No attempt has been made to describe the charm of his personality. That has been recognised long ago by the whole world: for many a year the ordinary restrictions of nationality have had little application to him; he has been venerated and acclaimed wherever scientific investigation is appreciated. No instance in his long career can be recalled in which he asserted for himself any claim of priority in intellectual achievement; rather his

attitude has always been to show how much he had learned from his colleagues, and how much he expected to derive from them in the future. In this regard it is fitting to interpolate an extract from the fine appreciation by Lord Rosebery, his successor in the Chancellorship of the University of Glasgow, delivered in his installation address\*: "In my personal intercourse with Lord Kelvin, what most struck me was his tenacity, his laboriousness, his indefatigable humility. In him was visible none of the superciliousness or scorn which sometimes embarrass the strongest intellects. Without condescension, he placed himself at once on a level with his companion. That has seemed to me a characteristic of such great men of science as I have chanced to meet. They are always face to face with the transcendent mysteries of nature. . . . Such labours produce a sublime calm, and it was that which seemed always to pervade Lord Kelvin. Surely, in an age fertile in distinction, but not lavish of greatness, he was truly great. Individualism is out of fashion. . . . But great individualities, such as Lord Kelvin's, are independent of the pressure of circumstance and the wayward course of civilisation."

It is unnecessary to attempt any list of the distinctions and awards which came to him in the course of years: it suffices to say that there was probably no honour open to a man of science that was not at his disposal. Abundant personal record is and will be available in appreciations by his colleagues, who were all his friends; for example, in the masterly estimate by G. F. FitzGerald, contained in the memorial volume reporting the proceedings in celebration of the Jubilee of his Professorship at Glasgow in 1899. In deference to the strikingly unanimous desire of his countrymen of all classes, and amid touching tributes from his colleagues in other nations, he was laid finally to rest in historic ground, on December 23, 1907, alongside his great exemplar, Sir Isaac Newton, in Westminster Abbey.

[J. L.]

\* The Times, June 13, 1908.

Friday, June 5, 1908.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. P.C. D.C.L.  
LL.D. F.R.S., President, in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,  
Fullerian Professor of Chemistry R.I.

*The Nadir of Temperature and Allied Problems.*

[ABSTRACT.]

MANY years ago the zenith of temperature and the intensity of solar heat were favourite subjects of mine, but since that time my investigations have led me to attack problems related to the nadir of temperature, and some of these I propose to consider in this discourse. Our absolute scale of temperature depends on gas thermometry; but for demonstration purposes thermojunctions coupled with reflecting galvanometers are more convenient.

On lowering a thermojunction into a vessel of liquid air, the galvanometer you observe registers  $88^{\circ}$  on the scale fixed on the wall in degrees absolute. On blowing air through the liquid scarcely any disturbance of the galvanometer is produced; when, however, hydrogen is bubbled through the liquid air, the galvanometer at once shows a lowering of temperature amounting to about  $5^{\circ}$ . On exhausting the liquid air, the temperature quickly falls and  $70^{\circ}$  absolute is registered, and in a short time the limit of  $65^{\circ}$  is reached, while the liquid air is boiling under a pressure of about 2 cm. mercury pressure.

If the liquid air is now replaced by liquid hydrogen, a temperature of  $20^{\circ}$  absolute is registered by the thermojunction, this being about the boiling point of the liquid. When the liquid hydrogen is rapidly exhausted, a fall is indicated to  $14^{\circ}$  or  $15^{\circ}$  absolute. The hydrogen has now solidified under a pressure of about 55 mm. Continuing the exhaustion on the solid hydrogen a temperature of  $13\frac{1}{2}^{\circ}$  is indicated. On admitting pure hydrogen at atmospheric pressure to the vacuum vessel, the solid hydrogen melts, and a temperature of  $20^{\circ}$  is once more registered.

The temperature of  $13^{\circ}$  absolute is the practical nadir; or the lowest temperature we can conveniently permanently maintain by the use of solid hydrogen.

Now hydrogen boils at  $20^{\circ}$  and air at  $88^{\circ}$ , which is more than four times as high. The temperature of the lecture room is about  $300^{\circ}$  absolute, that is fifteen times warmer than boiling hydrogen. Fifteen times higher than  $300^{\circ}$  gives a temperature of  $4500^{\circ}$ , which is nearly the temperature of the sun. We thus produce in the

laboratory a degree of cold relative to the average temperature which is exactly comparable to the intensely high temperature of the electric furnace or even that of the sun.

When liquid air is dropped on to the surface of fluids at the ordinary temperature, the liquid air at once assumes the spheroidal state, and rushes about on the warmer liquid which has a temperature three times higher. Projected by the lantern the liquid air drops look like tadpoles or nuclei with cometary tails formed of the condensing mist of the vapour of the warmer liquid. This experiment

was first shown some two years ago. If, now, liquid hydrogen is poured on to the surface of liquid air, the temperature ratio of the liquids being as great as 1 to 4, we anticipate the liquid hydrogen would equally float about in the spheroidal state. The experiment is quite successful although somewhat less striking than that of liquid air on the surface of carbon tetrachloride, because it all passes in a few seconds owing to the small latent heat of liquid hydrogen, although 10 c.c. of liquid hydrogen is used in each operation. The boiling liquid air surface is clouded over when the liquid hydrogen is poured on to it, owing to the formation of a snow of solid air, and all boiling of the liquid air is arrested. The rapidity of the passage of the phenomena is suggestive to some extent of the difficulties which surround experimental work when attempting to approach the nadir of temperature.

As an illustration of the importance of questions of radiation in low temperature research, two vacuum-jacketed vessels, alike in all respects except that one is coated inside with silver and the other with a film of highly reflecting lead sulphide (Fig. 1), are connected to the same liquid-air cooled charcoal exhaust, thereby ensuring and maintaining an identical high vacuum in each; and both afterwards charged with the same volume of liquid air. The air is allowed to distil from each vessel, and the rates of distillation compared. It takes thirty-five seconds for the silvered vessel to boil off a volume of air measured at the ordinary temperature of 50 c.c., while the lead-sulphide

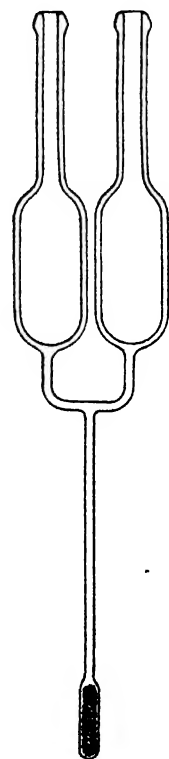


FIG. 1.

coated vessel only takes seven seconds to evaporate a similar amount. Thus the influx of heat from the sulphide of lead coated vessel is just five times greater than that entering by the silver covered surface. A film of nickel deposited from Mond's Nickel carbonyl is nearly as good as silver. Of course the influx of heat is not merely a question of radiation, but also involves gas convection; which again

depends on the perfection of the vacuum ; as well as heat conduction down the necks of the vessels.

All the oxygen used in London is now obtained from the fractionation of liquid air by the Linde method, and consequently is much purer than the old commercial oxygen, while substantially pure nitrogen can be obtained at the same time if wanted, along with the rare gases.

The cooling of air by adiabatic expansion is easily shown with an apparatus of the old Cailletet type, a thermojunction in the expanding air is connected to the reflecting galvanometer which shows the alterations of temperature on the scale fixed on the wall. The gas is compressed by the pump, cooled to absorb the heat of compression, and then suddenly expanded. Wroblewski in 1888 first saw a mist of hydrogen produced by this instantaneous method of cooling. With helium, I in 1901, and Olszewski, of Cracow, in 1905, both failed to observe any condensation by adiabatic expansion. The following table summarises the results of these experiments :—

ADIABATIC EXPANSION OF HELIUM AT TEMPERATURE OF  
SOLID HYDROGEN.

	Initial Pressure Atmospheres	Final Pressure. Atmospheres	Temperature. Degrees Cent. Absolute.	
			Olszewski, 1905.	Dewar, 1901.
Olszewski . . .	180	40	7·6	11·7
Dewar . . .	80 to 100	20	5·8	8·9
" . . .	..	10	4·4	6·7
" . . .	..	5	3·3	5·1
" . . .	..	1	1·7	2·7

Thus Olszewski thought he had reduced his temperature down to 1·7 degree above absolute zero, yet neither he nor I saw any indications of liquefaction. Olszewski, in fact, seemed to regard helium as possibly non-condensable, and such an inference, if true, would be an important addition to our knowledge. There are, however, several facts that would help to account for the failures to observe any condensation. The refractive index of helium and its latent heat are both very small, the latter probably only one-seventh that of hydrogen, so that it would be very difficult to see and isolate as a mist. When apparatus was arranged for helium circulation, similar to that used in the liquefaction of hydrogen, two difficulties arose, viz. the use of a sufficient amount of pure helium gas, and the supply of enough liquid hydrogen to maintain the cooling until regenerative action on the helium began. For the rapid liquefaction of hydrogen it is necessary to start from a temperature of 65°, and regenerate down to 20°. Assuming the boiling point of helium to

be about  $5^{\circ}$  (to which several observations of my own point) we must start from  $15^{\circ}$  to have the same temperature fall of 3 to 1. But that would require a large and elaborate plant, and with the mass of gases in circulation and the time required, the fight against any influx of heat from the outside becomes harder.

There is no intermediate fixed point between  $65^{\circ}$  and  $20^{\circ}$ , so that a descent of  $15^{\circ}$  has to be effected by regenerative methods in the liquefaction of hydrogen, and a similar rate of descent would have to be achieved before helium could be liquefied. In order to keep the circulation of helium up for four minutes in my apparatus, about 6 litres of hydrogen disappeared, and during all the time of the operation the impurities in the gas were accumulating at the valves.

There are other difficulties to be overcome before the apparatus could be worked with success. Hydrogen is cheap enough, helium very costly. For years our supply has come from the King's Well at Bath, which gives off a gas (largely nitrogen) containing  $\frac{1}{2000}$  of its volume of impure helium. We have to deal with very large volumes of gas, and after years of work I lost all my treasured store of helium. We know now that helium is more common than we had at first thought. Our atmosphere contains  $\frac{1}{200000}$  of helium, and in several springs it is more abundant than at Bath. The gases given off by certain springs in France contain more than 2 per cent. of helium. A similar amount has also been found in the natural gas of a North American town. With 100 or 200 litres of helium at the experimenter's disposal, it would be easy to prove the success or failure of the regenerative method.\*

For the present I have made further experiments on helium absorption by charcoal. With helium, the absorption only begins at the lowest realisable temperatures, but when we come to the boiling-point of hydrogen the charcoal absorbs 200 times its volume of helium, and the curve shows that helium at its own boiling-point of about  $5^{\circ}$  would most probably be absorbed to the same extent as hydrogen at its boiling-point. The absorption of gases by charcoal was accompanied by evolution of heat shown in the following table :

HEAT EVOLUTION DETERMINED BY CHANGE OF GAS TENSIONS AT DIFFERENT TEMPERATURES (CONCENTRATION CONSTANT) IN EACH EXPERIMENT.

	Molecular Latent Heat.	Temperature Absolute. Deg Cent.
Helium . . .	$4.6 \times 105$	18
Hydrogen . . .	$4.6 \times 114$	18
" . . .	$4.6 \times 436$	78
Nitrogen . . .	$4.6 \times 665$	82
Oxygen . . .	$4.6 \times 684$	82
Carbon dioxide .	$4.6 \times 1326$	180

\* Helium was liquefied by Professor Dr. Kamerlingh Onnes, of Leiden University, on July 9, 1908.

The direct value of the thermal evolution for hydrogen, about  $85^{\circ}$ , measured in the liquid air calorimeter described in last year's discourse, was found to be  $4.6 \times 426$ .

I showed in the last discourse the high exhaustions obtainable by the use of charcoal at low temperatures. The condensing action is still effective against considerable dynamic heats.

The following experiments illustrate this :

A very thin india-rubber membrane is stretched across the open end of a piece of glass tube 1 inch wide (being securely fixed by the use of melted rubber and thread to the outside wall of the tube) and connected to a discharge tube and a bulb containing charcoal which

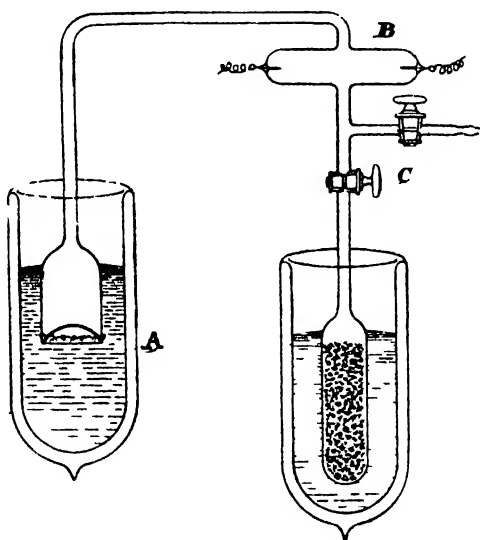


FIG. 2.

can be shut off by a stopcock (see A, B and C, Fig. 2). The apparatus is exhausted down to a few mm. pressure, thus forcing the rubber to be drawn out to a spherical shape, and the end of the tube is immersed in liquid air. A discharge is passed and the charcoal, already immersed in liquid air, is brought into play to increase the vacuum. The rate of diffusion through the membrane is so greatly diminished, that a vacuum is very soon produced by the charcoal which is so high that no discharge will pass. If the liquid air is taken away from A, a continuous discharge takes place in B owing to rapid diffusion through the rubber film at the ordinary temperature.

Measures on the rates of leakage across such membranes for a given surface in a given time were carried out by observing the increase of pressure in a McLeod gauge. The values are given in terms of the number of cubic millimetres of gas which passes per minute across an area of 1 square centimetre. Both air and hydrogen diffusion was examined. At ordinary temperatures the figures obtained were approximately 1.5 in air and 4.9 in hydrogen. At  $-80^{\circ}\text{C}$ . the corresponding values were 0.0009 and 0.0044, while at  $-185^{\circ}$

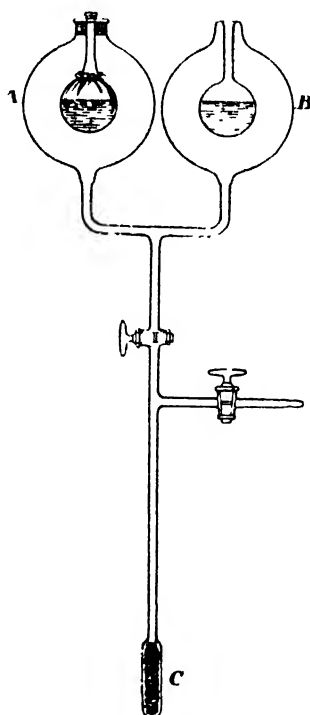


FIG. 3.

the figures were 0.00012 and 0.00013 respectively. One membrane was also tested while immersed in liquid hydrogen and was found to be quite tight.

An india-rubber vacuum vessel can be formed on a similar principle. Fig. 3 shows two little balloons, one of glass B, the other of a thin india-rubber membrane A, both within larger bulbs, which are connected together, the space within being maintained exhausted



by a charcoal bulb C. The vacuum so obtained is such that both little bulbs will hold liquid air without appreciable ebullition.

RELATIVE VISCOSITY OF AIR AT THE ORDINARY AND LIQUID  
AIR TEMPERATURES.

Referring to Fig. 4, A is a U-shaped quill tube filled with cotton wool and connected by stopcock D to B, which is a very fine capillary tube, drawn out in the blowpipe. C is an ordinary aluminium electrode

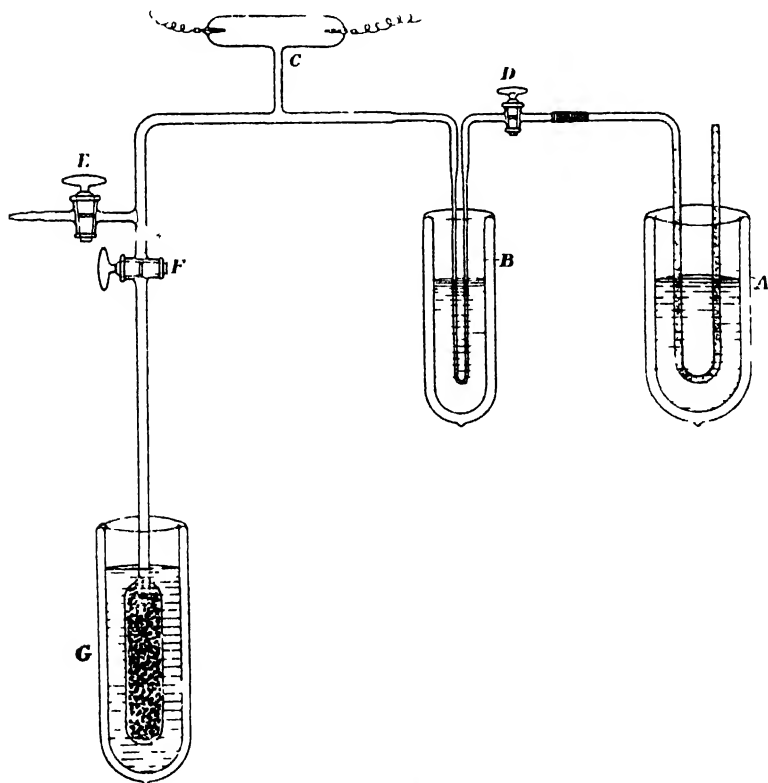


FIG. 4.

sparkling tube, used as manometer for indicating pressure in the apparatus by the alteration in the appearance of the electric discharge. E and F are stopcocks for exhausting the apparatus and connecting it to the charcoal condenser G. A is kept immersed in liquid air to

purify the entering gases. After the charcoal condenser is cooled, the vacuum in C becomes so high that the coil discharges across a 1-inch spark gap outside rather than through C. The stopcock D is turned to give a charge of dry air to fill the quill tube between D and the capillary B. The conductivity of C now becomes high, the outside spark gap stops acting, and the discharge again passes in C. The vacuum, however, rapidly becomes high until C begins to show a good glass phosphorescence. B is now cooled in liquid air, when a rapid leak of gas through B into C becomes apparent by the red glow of nitrogen round the positive pole through the viscosity of the air being reduced by the cooling, thus increasing the amount of leakage.

The converse experiment can be shown thus: when the vacuum is not low, e.g. just after turning D to admit a charge of air, we heat B with a spirit-lamp. The resistance in C now rapidly rises until sparks pass across the outside gap due to the high exhaust in C. When air is replaced by dried hydrogen the same phenomena can be shown.

The expression for the viscosity  $\mu$  of a gas at absolute temperature T is given by  $\mu = nT^a$  where  $n$  and  $a$  are constants. Rayleigh's value of  $a$  for air = 0.75, so that a change from 15° C. to -183° C. would diminish the viscosity  $2\frac{1}{2}$  times in any case. A series of quantitative experiments must be undertaken on the viscosity of hydrogen down to 20° absolute.

#### INCANDESCENCE OF A THORIA MANTLE PRODUCED BY CROOKES RAYS IN A CHARCOAL VACUUM.

A small piece of an ordinary gas mantle about 1 cm. square is supported by platinum wire near the focus of the concave aluminium cathode of a vacuum tube 15 cm. in length and 6 cm. diameter (Fig. 5). The platinum wire carrying the piece of Thoria mantle is fused into a glass rod B which can be pushed into any position by means of the indiarubber joint fitting B. As gases diffuse through the rubber tube at B a slight leak is maintained into the vacuum tube. The final exhaust is controlled by means of a side tube provided with a stop-cock and bulb containing 20 grm. of charcoal (G) placed in liquid air.

Starting with a few mm. pressure in the tube, the cooled charcoal is put into action by opening the stopcock. The pressure consequently falls, as indicated by the discharge. In a short time a dull red spot shows in the centre of the square of the mantle; this rapidly increases in intensity until a brilliant incandescence is obtained. Very soon however, as the pressure continues to fall by the action of the cooled charcoal, the incandescence again diminishes to a dull red spot and soon goes right out.

Now by closing the charcoal cock, the slight leak round the indiarubber joint causes the pressure again to rise in the tube and the

incandescence again establishes itself. The pressure still increasing, the incandescence again dies down and disappears. On opening the cock to the charcoal the same phenomena are again repeated.

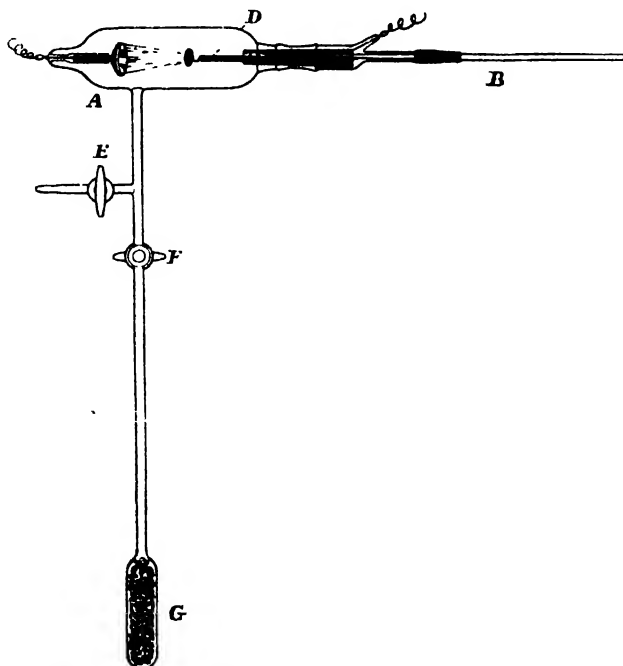


FIG. 5.

The limits of pressure, as measured by a McLeod gauge, within which this incandescence occurs range from  $0.03$  mm. to  $0.003$  mm.

#### SOLID HYDROGEN BY CHARCOAL EXHAUST.

A liquid may be solidified by the aid of a charcoal condenser maintained at four times its absolute boiling point. A vacuum tube (Fig. 6) containing liquid hydrogen A is surrounded by another vessel of liquid air B, arranged for projection, care being taken to guard against heat radiation from the electric lamp by the use of a water cell. A large bulb of charcoal C, cooled in a separate vessel of liquid air F, is connected to a bent tube provided with a three-way stopcock D, passing through an india-rubber cork E which fits the liquid hydrogen vacuum tube A. The cork is now rapidly fitted

into the neck of the liquid hydrogen tube, and the stopcock opened to the charcoal condenser. The liquid hydrogen is thus subjected to the exhaust of the large cooled charcoal bulb, and is seen to boil up rapidly, and very soon opaque solid hydrogen appears in ever-growing amount, until the whole mass of hydrogen is frozen to a snowy froth.

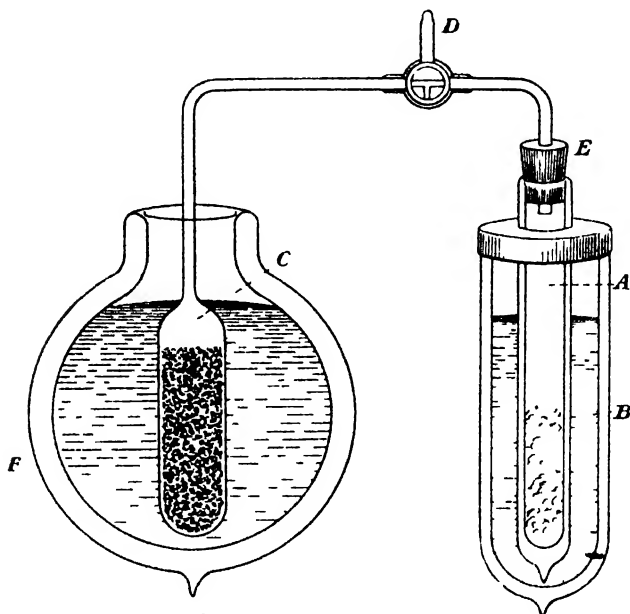


FIG. 6.

In this connection it may be pointed out that assuming the temperature of boiling helium to be about  $5^{\circ}$  absolute, then charcoal in liquid hydrogen under exhaustion, along with proper isolation of the helium from influx of heat, would very probably be able in a similar manner to bring about the production of solid helium, and we may be certain that if the charcoal could be cooled in liquid helium, then it could be solidified even if its solid tension was exceedingly small.

[J. D.]

## HODGKINS TRUST.

ESSAY BY PROFESSOR HENRY E. ARMSTRONG.

### *Low-Temperature Research at the Royal Institution, 1900-1907.*

IN the account given, in 1901, by Miss Agnes Clerke, of Low-Temperature Research at the Royal Institution during the years 1893-1900,\* the achievements chronicled included the solidification of oxygen, the liquefaction of fluorine and the liquefaction and solidification of hydrogen; the only gas remaining uncoerced was helium.

During the period 1900-1907, of which the present account is in a measure a record, siege has constantly been laid to the formidable entrenchments behind which this gas was established; the few who have been privileged to follow the work are aware that operations have been carried on with all the ingenuity and tenacity of purpose which have characterised previous attacks on the gaseous state made in the laboratory of the Institution. But the difficulties met with have been many and great; moreover, progress has been much hampered by Sir James Dewar's continued ill-health and—the confession is a sad one to make—of late especially by lack of funds. Another circumstance has delayed the prosecution of the attempt to degrade helium from its virtuous position as gas: genius has been defined as the capacity for taking pains, and doubtless one of the qualities of genius is perseverance in pursuit of an object, when intuition does not carry it straight to the mark; a more distinguishing feature is the artistic longing for novelty of effect and its manifestation in new works: it is a striking fact that elsewhere liquefied gases have been utilised practically only as mere cooling agents; at the Royal Institution an extraordinary variety of new applications have been made of the intense frigorific effects there available: the aim constantly in view has been not merely to improve the appliances but to develop the use of liquefied gases to the solution of the manifold problems involved in the study of the properties of matter at excessively low temperatures. The period under review has been almost more productive than any previous period from this point of view, one contribution of superlative importance having been made which has both revolutionised practice in the region of low vacua and extended to an altogether remarkable extent our power of dealing with gases and discriminating between

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\* A summary of the work carried on with the aid of the Hodgkins Trust is, by the authority of the Managers, incorporated in the Proceedings of the Royal Institution every seven years.



SIR JAMES DEWAR

PORTRAIT TAKEN IN THE LABORATORY IN THE SUMMER OF 1902 BY DR. A. SCOTT

them. The first septenate may be termed *the Hydrogen period*\*; the second *the Charcoal Vacuum period*. The discovery of the marvellous power of charcoals to absorb gases at low temperatures will render this latter period ever memorable.

The reduction of helium from the gaseous state became practicable only when this discovery was made, but to utilise such a new appliance fully was not easy; naturally others have entered the field meanwhile and success has fallen to those who have completest command of the necessary appliances and the ample funds, as well as the skilled assistance, required for the rapid prosecution of such work.

#### THE USE OF CHARCOAL IN THE PRODUCTION OF HIGH VACUA.

Charcoal, it has long been known, even under ordinary conditions, has the power of absorbing gases and vapours, often in considerable proportions; it is noteworthy also that it is commonly used in depriving liquids of colour—on a very large scale, for example, in purifying sugar. The desire to explain its absorptive power has given rise to much experimental inquiry; indeed, of late years, the property which charcoal possesses, in common with many other materials in a fine state of division, including soils, of withdrawing substances from solution has been the subject of many discussions.

In sketching the history of the subject in 1905, Sir James Dewar pointed out that speculations on the porosity of matter date back several centuries. He drew attention to the following significant passage in a discourse published in 1684 by Boyle and entitled “Experiments and Considerations about the Porosity of Bodies” :—

“When I consider how much most of the qualities of bodies and consequently their operations depend upon the structure of their minute and singly invisible particles and that to this latent contexture, the bigness, the figure and the collocation of the intervals and pores do necessarily concur with the size, shape and disposition or contrivance of the substantial parts, I cannot but think the doctrine of the small pores of bodies of no small importance to Natural Philosophy.”

Modern inquiry has thoroughly justified Boyle's acute surmise that “the qualities of bodies and consequently their operations” are functions of their latent contexture,† organic chemistry being one

\* It should not be forgotten that the Dewar vacuum vessel came into use during this period and was proved to be indispensable to the successful prosecution of inquiry at low temperatures; that period may therefore well be ranked also as the vacuum vessel period.

† Contexture—“the disposition and union of the constituent parts of a thing with respect to each other: constitution”; as an apposite expression of internal structure, the term may be preferred to configuration, which is now commonly used.

continuous proof of the accuracy of his contention : achievements such as the production of the natural colouring matters (the madder colours, indigo, etc.) by artificial means are entirely the outcome of the command secured by chemists through their studies of the internal structure of molecules and of function as determined by structure. Yet it must be confessed that the doctrine of the small pores of bodies is but beginning to attract the share of attention which is due to its importance, especially in relation to the properties of soils.

Priestley, the pioneer investigator of different kinds of air, in the third volume of his "Experiments and Observations relating to various branches of Natural Philosophy," published in 1786, refers to "the property that charcoal has of absorbing air" as "a remarkable circumstance first observed by the Abbé Fontana, physicist to Duke Ferdinand II. of Tuscany"; and he also speaks of having repeated the Abbé Fontana's experiments by introducing hot charcoal through mercury into vessels containing different kinds of air. Priestley, indeed, seems to have been made acquainted with the power that heated charcoal has of absorbing gases by Fontana himself in 1770.

That the subject attracted attention at about the beginning of last century is clear from a statement made by Dalton in his "New System of Chemical Philosophy" (1810, part ii. p. 235) :-

"Several authors have maintained that charcoal after being heated red has the property of absorbing most species of elastic fluids in such quantities as to exceed its bulk several times; by which we are to understand a chemical union of the elastic fluids with the charcoal. The results of their experiments on this head are so vague and contradictory as to leave little credit even to the fact of any such absorption. I made 1500 grains of charcoal red hot, then pulverised it and put it into a Florence flask with a stopcock; to this a bladder filled with carbonic acid was connected; this experiment was continued for a week and occasionally examined by weighing the flask and its contents. At first there appeared an increase of 6 or 7 grains from the acid mingling with the common air in the flask of less specific gravity; but the succeeding increase was not more than 6 grains and arose from the moisture which permeated the bladder: for the bladder continued as distended as at first and finally upon examination was found to contain nothing but atmospheric air. Yet carbonic acid is stated to be the most absorbed by charcoal. One of the authors above alluded to asserts that the heat of boiling water is sufficient to expel the greater part of the gases so absorbed. Now this is certainly not true, as Allen and Pepys have shown; and most practical chemists know that no air is to be obtained from moist charcoal below red heat. Hence the weight acquired by fresh made charcoal is in all probability to be wholly ascribed to the moisture which it absorbs from the atmosphere; and it is to the decomposition of this water and the union of its elements with charcoal that we obtain such an abundance of gases by the application of a red heat."

In view of the crudeness of Dalton's methods, it is perhaps not



surprising that he failed even to confirm the observations of earlier workers.

The subject was first dealt with in a thorough manner by Theodore de Saussure in 1812. An English translation of his important memoirs is to be found in the "Annals of Philosophy," vol. vi. pp. 241-255, 331-347. In his experiments red-hot box-wood charcoal was plunged under mercury and introduced into the gas to be absorbed after it was cool and without ever coming into contact with atmospheric air. He gives the following table :—

Charcoal of Box-wood Absorbs, of	Volumes.
Ammoniacal gas . . . . .	90
Muriatic acid . . . . .	85
Sulphurous acid . . . . .	65
Sulphureted hydrogen . . . . .	55
Nitrous oxide . . . . .	40
Carbonic acid . . . . .	35
Olefiant gas . . . . .	35
Carbonic oxide . . . . .	9.42
Oxygen . . . . .	9.25
Azote . . . . .	7.5
Oxy-carbureted hydrogen . . . . .	5
Hydrogen . . . . .	1.75

De Saussure showed that the property of absorbing gases was common to all porous solids but found no substance possessing the property in so high a degree as charcoal. He arrived at interesting results with mixtures of gases and proved the incorrectness of the statement made by Rouppe and Norden that water was formed by the interaction of hydrogen and oxygen when these two gases were absorbed by charcoal. The volume of gas expelled from charcoal by another gas was found to vary according to the proportion in which both gases exist in the unabsorbed residue. In several cases, the presence of one gas in the charcoal was found to facilitate the condensation of the other.

An interesting series of communications was made to the Chemical Society during the "sixties" by John Hunter. Besides confirming De Saussure's observations, he described the results of measurements of the absorption by charcoal at temperatures extending up to 200° C. not only of gases but also a large number of vapours. Hunter showed that logwood, ebony and cocoanut charcoal exceed that from boxwood in absorptive power, the very dense variety prepared from cocoanut being superior to all other forms.

Charcoal has been used in respirators as a protection against infection; it has been enclosed in covers placed over the openings of sewers to prevent the escape of noxious emanations into the streets; its value as a means of purifying drinking water has long been recognised; but no scientific application was made of its extraordinary power of condensing and holding gases until recently:

Professors Tait and Dewar, in 1874-5, were the first to recognise and take advantage of the property it has of retaining them even under very low pressures. A brief account of their work was published, under the title "On a New Method of obtaining very Perfect Vacua," in the 'Proceedings of the Royal Society of Edinburgh' (1875, viii. 348, 628) and also in 'Nature' (1875, xii. 217). The method consisted in heating charcoal to redness in a tube attached to a mercury pump while the exhaustion was proceeding and to seal the vessel when this was completed. When the charcoal was cold the vacuum was found to be so complete that, even when a powerful coil was used, no spark would pass between platinum wires sealed into the tube only one-fourth of an inch apart. The account referred to is of special interest also as containing a noteworthy contribution to the theory of that most wonderful of instruments the *Radiometer*, the discovery of which by Sir William Crookes has been the point of departure for all modern research on the phenomena of high vacua.

In closing their communication to the Royal Society of Edinburgh, Professors Tait and Dewar remark:—

"We need hardly say that this easy means of obtaining high vacua will be of importance in spectroscopic observations and we intend shortly to communicate observations in this direction."

Nevertheless the method remained undeveloped until 1904 and was then resuscitated almost by accident—which is but another illustration of the manner in which the obvious is neglected until, for some reason, it compels attention. Sir James Dewar had made experiments with finely divided platinum and palladium, which are known to occlude gases, in particular hydrogen and oxygen, even at ordinary temperatures and to take up larger quantities when heated. Finding that their absorptive power was but little affected by cooling, he bethought himself of charcoal and proceeded to contrast its behaviour with that of the metals before mentioned. The momentous discovery was then made that when cooled by liquid air charcoal has an altogether extraordinary power of condensing gases.

Those who have attended the lectures at the Royal Institution during the period under consideration are aware that this has been demonstrated in the most striking manner possible and in a great variety of ways.

All charcoals possess the property. The light variety used in making gunpowder or that prepared by carbonising blood both act; that made from cocoanut, however, is the most effective variety for general use.

The difference in the behaviour of various gases with cocoanut charcoal at  $0^{\circ}$  and at  $-185^{\circ}$  is well shown in the following table, in which the results are recorded of a series of experiments made with one and the same portion of charcoal, the volume absorbed being

that of the gas measured at 0° and under a pressure of 760 mm. of mercury :—

	I. Volume absorbed at 0° C.	II. Volume absorbed at -185°	III. Ratio of I. to II. :
Helium . . . .	2 c.c.	15 c.c.	7.5
Hydrogen . . . .	4	135	34.0
Electrolytic gas . . . .	12	150	12.5
Argon . . . .	12	175	14.6
Nitrogen . . . .	15	155	10.3
Oxygen . . . .	18	250	12.8
Carbonic oxide . . . .	21	190	9.0
Carbonic oxide and oxygen	30	195	6.5

These observations were made at an early stage of the inquiry. Afterwards it was found that the quality of the charcoal depends much on the way in which it is prepared and that the absorptive power is enhanced by carbonising the cocoanut shell slowly at a gradually increasing temperature; whereas the specimens at first used absorbed only about 150 c.c. of air per gramme at -185°, those prepared subsequently with these precautions absorbed from 350 to 400 c.c. per gramme. Porous materials other than charcoal, such as alumina, meerschaum and silica, also absorb an increased proportion of gases at low temperatures but their retentive power is much inferior to that of charcoal, which clearly has a special power.

Pressure has but relatively little influence in increasing the amount of gas absorbed. Thus in one case it was observed that 6.7 grammes of a particular specimen of charcoal would not absorb more than 1 litre of hydrogen, even when the pressure was raised from 10 to 25 atmospheres, the amount taken up having reached a limit at the lower pressure and being then less than double what it was at ordinary atmospheric pressure.

*Absorption of a Mixture of Gases by Charcoal.*—One of the most interesting series of observations made is that relating to the equilibria established on saturating charcoal at low temperatures with a mixture of gases. Charcoal which has been heated, exhausted and then allowed to absorb ordinary air at -185° presumably contains within its pores a mixture approximately of the composition represented by Fig. 1.

If, at the same low temperature, a stream of air be passed slowly and continuously over the charcoal, at first almost pure nitrogen escapes, showing that the system has a preference for oxygen; after several hours, however, the occluded gas has a new and apparently definite composition. On displacing the whole of the gas from the charcoal, a mixture is obtained containing on the average about 60 per cent. of oxygen, corresponding nearly to Fig. 2.

If the charcoal saturated with such a mixture be subjected in a similar manner to the action of a slow current of hydrogen, about

one out of every five of the molecules of oxygen and nitrogen ( $3 + 2$ ) is displaced by hydrogen, giving rise to the system represented by Fig. 3. When charcoal saturated with oxygen is exposed in hydrogen, the composition of the mixture finally occluded is about that represented by Fig. 4; whilst if it act on charcoal saturated with nitrogen it gives rise to the system represented in Fig. 5. Lastly, if air be passed over charcoal saturated with

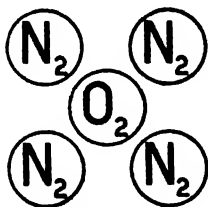


FIG. 1.

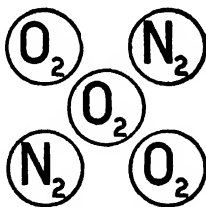


FIG. 2.

hydrogen, the whole of the latter is ultimately displaced, the occluded gas being of the composition represented by Fig. 2.

It is clear from these observations that the more volatile or less condensable the gas, the less it is absorbed and retained in the charcoal. Charcoal may therefore be made use of most effectively in separating the constituents of a mixture of gases of different degrees of volatility.

In the perfectly gaseous state, at and above the critical temperature, the molecules of a substance are free from mutual control. In the liquid state the molecules are in a state of what may be termed

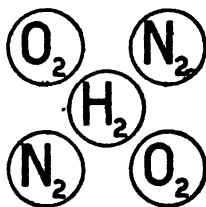


FIG. 3.

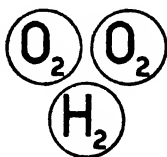


FIG. 4.

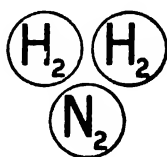


FIG. 5.

shifting association, their vibratory activity being so much reduced that they are able to cling together during an appreciable interval of time in virtue of the surplus or residual affinity with which they are endowed. In the passage from the one state into the other, an increasing proportion passes from the condition of freedom into that of limited association or *vice versa*, according as the temperature falls or rises. A liquid, therefore, always has a certain attraction for the gaseous molecules of its own kind with which it is surrounded; the passage from the one state into the other may be regarded not

as a mere physical change but as a chemical change, inasmuch as it involves a change in the number of kinetic units, in other words, in molecular composition, such as is exemplified by the expression  $xM \rightleftharpoons M^x$ .

In a solid, the association of the molecules which are the units in the gas is of a rigid character; so soon as they oscillate outside certain mean positions, the mass ceases to be solid and passes into either the viscous fluid or the liquid state.

When charcoal is brought into contact with a gas, presumably its surfaces become coated initially with a layer of molecules which may be regarded as practically solidified. If the temperature be low enough, this surface layer of molecules attracts other molecules, thus forming the equivalent of a liquid layer. The office of the charcoal may therefore be supposed to be that of acting, in virtue of its rigidity and its affinity, as an anchorage, as it were, for the molecules which are presented to it in the gaseous state; once anchored, these molecules can exercise their blandishments over their own kind in a manner which is impossible so long as they are flying about violently in every possible direction.

*Density of Gases Absorbed in Charcoal.*—As Sir James Dewar points out, the surface presented by charcoal is enormous. According to Mitcherlich, the cells of charred wood are on an average  $\frac{1}{2400}$  of an inch in diameter. A cubic inch of charcoal cut up into small equal cubes having edges  $\frac{1}{2400}$  of an inch long would offer a surface area of 100 square feet; taking into account, however, the space occupied by the charcoal itself, the area would be about 73 square feet. If the amount of carbon dioxide absorbed by such an amount of charcoal under ordinary conditions were spread as a liquid over such an area, the thickness of the layer would be about 0.000002 of an inch.

Taking into account the real and apparent density of charcoal such as has been used, the average pore space in 100 grammes may be taken as being about 15 cubic centimetres. Calculating with the aid of this value the average density of the material condensed within the charcoal and contrasting it with that of the liquid obtained on condensing the gas alone, it seems that the density of the absorbed material is equal if not a little superior to that of the same substance in the liquid state at the same temperature. The results are given in the table opposite.

It will be noted that the density of the occluded hydrogen at 80° absolute is practically that of liquefied hydrogen; as this temperature is about four times that at which hydrogen boils, the density of the occluded helium at 15° absolute being 0.17, it may be inferred that this would be about the density of liquid helium at its boiling point, about 4° absolute. Actually, Prof. Onnes has found the density of liquid helium at about 4.5° to be 0.15.

Gas.	Temperature of Absorption.		Density of Gas occluded in Charcoal.	Density of liquefied Gas.
	Cent.	Abs.		
Carbon dioxide .	+ 15°	288°	0·7	0·8
Oxygen . . .	- 183	90	1·83	1·12
Nitrogen . . .	- 183	80	1·00	0·84
Electrolytic gas .	..	..	0·58	?
Hydrogen . . .	- 193	80	0·06	0·07
Hydrogen . . .	- 210	63	0·08	..
Hydrogen . . .	- 252	21	0·11	..
Helium . . .	- 258	15	0·17	0·15

PERFECTION OF VACUA OBTAINED BY MEANS OF HIGHLY-COOLED CHARCOAL.—SEPARATION OF GASES.

The perfection of the vacuum obtained by means of charcoal at low temperatures is readily demonstrated with the aid of a sparking tube C A B, such as is shown in the left-hand side of Fig. 6, C being a bulb containing cocoanut charcoal. When such a tube of 1300 c.c. capacity, sealed to a bulb containing 30 grammes of charcoal, was filled with air at atmospheric pressure and then cooled by immersing the charcoal bulb in liquid air, the pressure fell to 50 mm. of mercury : when, however, the tube was filled at the pres-

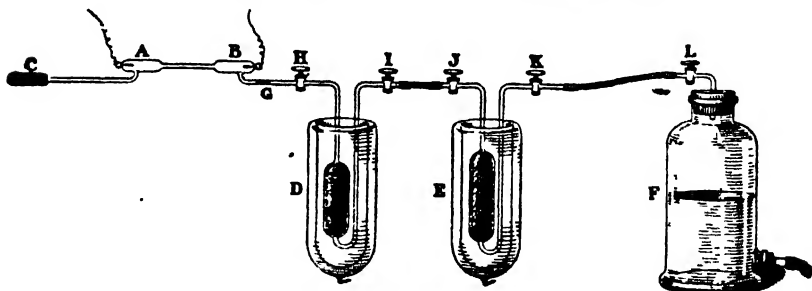


FIG. 6.

sure of only half an atmosphere, on cooling the charcoal to  $-185^{\circ}$ , the exhaustion reached beyond the striæ stage ; and no spark would pass when the initial charge was only at the pressure of a quarter of an atmosphere. Using a tube containing only 1 gramme of charcoal and charging it with air at a pressure of 3 mm. of mercury, the vacuum produced on cooling the charcoal just reached the beginning of the phosphorescent stage. Starting with an air pressure of between 1 and 2 mm. a volume of 300 c.c. connected with a tube containing 5 grammes of charcoal cooled in liquid air can reach a vacuum of 0·00005 mm. in one hour.

When the tube was charged with hydrogen, to raise the vacuum

to the striæ stage it was necessary either to use a larger amount of charcoal or to reduce the pressure of the gas to less than an atmosphere; but on lowering the temperature of the air bulb to  $-210^{\circ}$ , by boiling off the air, the exhaustion in the tube just reached the beginning of phosphorescence round the cathodes. Helium was absorbed to but a very slight extent; neon more readily.

In tubes charged with air, it is easy to observe the gradual disappearance of the spectra of oxygen, nitrogen, etc., in the order of the volatility as the exhaustion proceeds; the F line of hydrogen and the yellow line of neon are always noticeable, so that the test for the latter gas is a very delicate one, as the amount of neon in the air cannot well exceed  $\frac{1}{1000}$ .

To obtain a satisfactory spectrum of helium, it is necessary to enrich the air in the sparking tube. Fig. 6 shows the apparatus used for the purpose. In an experiment in which 200 c.c. of air were supplied to the tube D containing 15 grammes of charcoal cooled by liquid air, on passing the residue on to the sparking tube and examining it spectroscopically, the lines seen were the C and F lines of hydrogen, the yellow and some of the orange lines of neon and also the yellow and green lines of helium. On using the residuary gas from a litre of air, all the helium lines were seen, as well as the yellow neon and the F line of hydrogen—from which it may be inferred that  $\frac{1}{1000}$  part of helium by volume may be detected.

As 40 to 50 grammes of charcoal at the temperature of liquid air can absorb from 5 to 6 litres of air, it is easy to accumulate the more volatile gases for spectroscopic examination by using the two condensers E and D shown in Fig. 6. As soon as the charcoal in E is nearly saturated and the less condensable gas has been transferred to D by closing the cock K and opening J and I, the condenser E is removed and rapidly raised to the air temperature, so as to expel the condensed gas; it is then replaced in the circuit and used as before. 50 litres of air can be treated in this manner within a short time; sparking tubes charged with the residuary gas show brilliant spectra of all the more volatile constituents of air.

A variety of interesting demonstrations of a similar kind illustrating the differential condensation of gases by charcoal have been given by Sir James Dewar, such as the separation of the gaseous products from minerals and radio-active bodies, the gases dissolved in rain, well and river waters, together with samples taken from the ocean. Speaking generally, the lower the boiling-point, that is to say the less condensable it is, the less a gas is absorbed.

Krypton and xenon are readily separated from air either by passing a current of air (purified by cooling it with liquid air) over charcoal cooled to  $-183^{\circ}$  or by covering a few hundred grammes of charcoal with old liquid air and allowing this to evaporate in a silvered vacuum vessel, then allowing a further quantity of the retained air to escape from the charcoal at the temperature of solid carbon dioxide, finally extracting the residual gas from the charcoal

and purifying it from carbon compounds and oxygen. The remaining mixture of nitrogen with krypton and xenon is separated into its constituents by condensation and fractionation.

No more effective demonstration of the extraordinary absorptive power of charcoal could well be imagined than that given at the Friday evening lecture in June 1908, when liquid hydrogen (surrounded by liquid air) was solidified in the course of very few minutes by the cold produced by its own evaporation, this being brought about by means of charcoal cooled by liquid air. The arrangement was that of a cryophorus in which the one bulb contained liquid hydrogen the other charcoal.

*Evolution of Heat on Absorption of Gases by Charcoal.*—When gases are condensed by charcoal the amount of heat liberated is considerably in excess of that which necessarily attends the passage from the gaseous into the liquid state. The first values deduced by Sir James Dewar are as given below, those in the middle column of figures being the amounts of heat (in gramme calories) liberated by the mere liquefaction of gramme molecular proportions of the gases, those in the last the amounts liberated when the same quantities of gas are condensed by charcoal at the temperature of liquid air:—

	Molecular Heat of Liquefaction. Calories.	Molecular Heat of Absorption. Calories.
Hydrogen . . . . .	238	1600
Nitrogen . . . . .	1372	3684
Oxygen . . . . .	1664	3744
Argon . . . . .	..	3636
Carbonic oxide. . . . .	..	3416
Carbonic oxide and oxygen (equal volumes) . . . . .	..	3960
Electrolytic gas . . . . .	..	2414

The surprising fact brought out by these figures is that hydrogen, although the least condensable gas, is that which has the greatest affinity for charcoal. The behaviour of helium, however, is even more remarkable. When hydrogen is absorbed at  $-185^{\circ}$ , it is at a temperature about four and a half times its boiling-point ( $20^{\circ}$  abs.); but helium is being absorbed at a temperature between fifteen and twenty times its boiling-point ( $5^{\circ}$  abs.). To make a fair comparison, hydrogen should be taken at a temperature at least fifteen times its boiling-point, so that the absorption of helium at  $-185^{\circ}$  C. should be contrasted with that of hydrogen at  $0^{\circ}$  C. It was therefore to be inferred that at  $15^{\circ}$  to  $20^{\circ}$  absolute helium would be condensed to a more remarkable extent than hydrogen at  $-185^{\circ}$ ; the following figures showing the number of volumes of the two gases condensed by the charcoal are proof of the accuracy of this conclusion:—

Temperature.	Helium.	Hydrogen.
- $185^{\circ}$ C. (boiling-point of liquid air) . . . . .	2½	187
- $210^{\circ}$ C. (liquid air under exhaustion) . . . . .	5	180
- $252^{\circ}$ C. (boiling-point of liquid hydrogen) . . . . .	160	268
- $258^{\circ}$ C. (solid hydrogen) . . . . .	195	..



As the relation between the volume absorbed and the temperature is nearly lineal in the later stages of the condensation of hydrogen and helium, it may be inferred that at a temperature of from  $5^{\circ}$  to  $6^{\circ}$  absolute helium would be as freely absorbed by charcoal as hydrogen is at its boiling point, so that, in all probability, the boiling point of helium is not below  $5^{\circ}$ . That such an inference is legitimate cannot be denied in view of the fact that at the boiling points of liquid hydrogen, nitrogen and oxygen respectively, good charcoal absorbs (at atmospheric pressure) equal volumes of each of these gases, namely 260 c.c. per gramme. It is to be noted that the rate

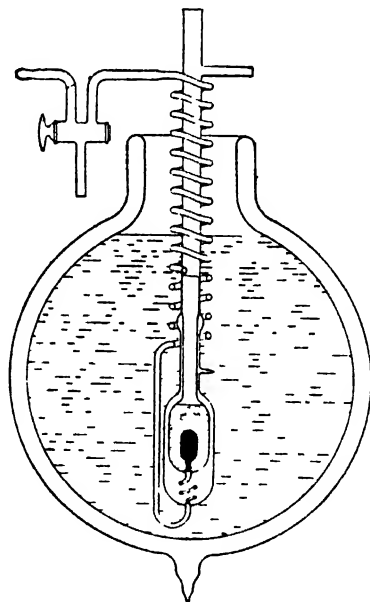


FIG. 7

at which helium is absorbed increases far more rapidly than does that of hydrogen, a degree or two making a great difference in the volume absorbed. Judging from such results therefore, it was highly probable that the boiling point of helium is about one-fourth that of hydrogen just as that of hydrogen is about one-fourth that of nitrogen.

The heat values given above are those deduced from an early series of experiments. Later, more refined determinations made with the apparatus depicted in Fig. 7 (which is a modification of the liquid air calorimeter suitable for this investigation) show that at  $18^{\circ}$  absolute the molecular latent heat of absorption of helium in charcoal, 483 calories, is nearly equal to the molecular heat of hydrogen absorption

in charcoal, 524 calories at 20° absolute. As at 78° abs. the molecular latent heat of absorption of hydrogen in charcoal is 2005 calories, a value about four times as great as that determined at about one-fourth the temperature, it may be inferred that the molecular latent heat of absorption of helium at its boiling-point, supposing this to be about 5° absolute, would be about one-fourth the value observed at 18°, viz.  $\frac{483}{4} = 120$  calories. As the amount of heat given out in the liquefaction of a gramme molecular proportion of hydrogen at its boiling-point is about half as great as that given out when it is absorbed by charcoal at the same temperature, by analogy it may be inferred that the molecular heat of liquefaction of helium at its boiling-point would be about  $\frac{120}{2} = 60$  calories. Knowing the latent heat, the boiling-point, and the fluid density from the helium charcoal absorption experiments, assuming by analogy a similar behaviour to that of other gaseous elements, all the data are available to calculate the vapour pressures of liquid helium.\*

As bearing on the properties of the hydrogen and helium molecules, these results are of extraordinary significance. It is clear that when cooled to a temperature at which their motility is so much reduced that they are no longer indifferent to other molecules, they are possessed of powers of attraction which are by no means inconsiderable.

#### METALLIC VACUUM VESSELS.

One great advantage attaching to the use of charcoal is that it has rendered possible the maintenance of a very high vacuum during any required period of time. In the pre-charcoal period, this was impossible, owing to the leakage of gas into the exhausted vessel either as a consequence of the mechanical imperfection of the glass vessel or because of the existence of air imprisoned in bubbles or tubules within the glass: such leakage may now be counteracted by means of charcoal.

Metallic vacuum vessels could not be made formerly for a similar reason, the gas occluded within the metal escaping gradually and spoiling the vacuum in the vessel. By enclosing a quantity of charcoal in a globular space A (Fig. 8), so that it is cooled by the liquid air in the inner vessel, this difficulty is entirely obviated: such metallic vessels are now made of nickel, brass or copper, provided with necks made of an alloy of low conducting power. When properly constructed, these vessels are as effective as chemically silvered glass vacuum vessels; as they are not fragile like the glass vessels, it is to be expected that they will be of the greatest service in future work with liquefied gases.

The manufacture of Dewar vacuum vessels is now a German

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\* The following formula gives an approximation to the vapour pressure in mm.; T being the absolute temperature log:  $P_{He} = 5.324 - 11/T$ . A similar formula for liquid hydrogen gives log  $P_H = 5.778 - 54.6/T$ .

industry of considerable magnitude; it is well known, in fact, that under the name of "Thermos flasks" they are now in popular use both for storing hot beverages and for keeping liquids cold in summer time. In view of the importance of food being always

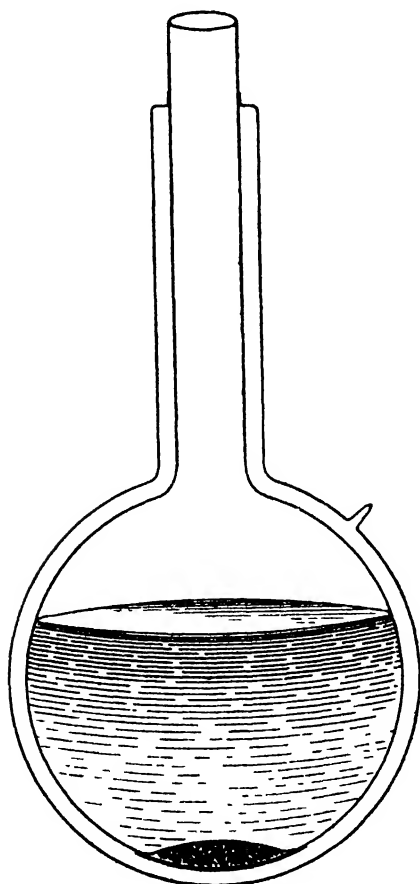


FIG. 8.

administered to infants at an even temperature, the use of such flasks may be expected to become very general. This is one illustration of the way in which the research work of the Royal Institution has conduced to the realisation of the objects of its founder, Count Rumford.

## PROPERTIES AND STRUCTURE OF CARBON.

The differences, which are both qualitative and quantitative, between various kinds of charcoal depend probably both on differences in porosity and on differences in composition. Charcoal is by no means a single substance but contains more or less hydrogen, oxygen and nitrogen; the amount of actual carbon, in an uncombined form, which is present in it cannot even be surmised.

Analyses of blood charcoal, for example, show that it may contain nearly 2 per cent. of hydrogen, 7 of nitrogen and 15 of oxygen, together with about 6 per cent. of mineral matter. Soot will contain over 60 per cent. of carbon, together with 7 or 8 of oxygen. Sugar charcoal may contain nearly 20 per cent. of oxygen.

Whatever the composition of charcoal may be, even if it consist entirely of compounds which are all but carbon, its properties are very nearly those of carbon in the amorphous state. It is therefore desirable to consider the peculiarities of amorphous carbon in elucidation of the remarkable power which charcoal possesses of attracting gases. In view of the very different behaviour of the three forms of carbon, it is almost certain that in the amorphous state it offers structural peculiarities which condition its special activity as an absorbent: there are two points of view, from which these peculiarities may be considered with advantage—the one being that of the genetic relationship of charcoal to carbon compounds, especially the hydrocarbons, the other that of its colour.

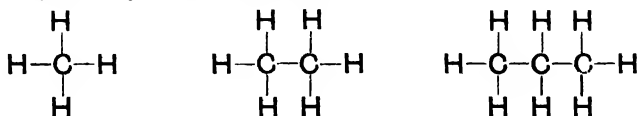
*Genesis of Amorphous Carbon.*—Of all the elements, carbon is the most remarkable on account of the endless multiplicity of compounds to which it gives rise, over 130,000 being already known. The properties of the element are to be inferred from the study of this vast host. By considering the peculiarities, by contrasting and correlating the idiosyncrasies of the various compounds, the chemist is eventually enabled to paint a picture of the ideal substance symbolised by the letter C—the symbol significant of the carbon unit or atom; that is to say, of the elementary material carbon but not of any of the forms of carbon actually known to us, the presumption being that these are all substances of great molecular complexity the formation of which is a consequence of peculiarities inherent in the carbon atom.

The potentialities of the carbon atom are best elucidated by reference to the behaviour of the hydrocarbons—the compounds formed by the association of hydrogen with carbon. The simplest of these, which is represented by the formula  $\text{CH}_4$ , methane or marsh gas, is a *saturated* compound; nothing can be combined with it but one or more of the hydrogen atoms it contains may be displaced by another radicle of equivalent value in combining power—chlorine or bromine or iodine, for example. Taking the hydrogen atom as the unit, the atom fixing power or *valency* of carbon is indicated by the fact that

in methane the single carbon atom is satisfied by and in turn satisfies four single separate atoms of hydrogen—in other words, it is quadri-valent or tetradic.\*

Methane is but one of a long series of hydrocarbons all of which contain carbon and hydrogen in the same relative proportions—those expressed by the formula  $C_nH_{2n+2}$ , as there are twice as many atoms and two more of hydrogen as of carbon in the molecule of each hydrocarbon. The petroleum pumped from the oil wells in Pennsylvania and elsewhere is a very complex mixture of such hydrocarbons, the natural gas from the same wells consisting of methane and other gaseous terms of the series; petrol, which now plays so important a part in motor practice, is a mixture of the lower liquid terms, such as *pentane*,  $C_5H_{12}$ , *hexane*,  $C_6H_{14}$ , *heptane*,  $C_7H_{16}$ ; the petroleum or paraffin oil used in lamps consists for the most part of much higher terms of the series; the mineral lubricating oils which have rendered such service in the high pressure steam engine, the unguent vaselin and the solid paraffin wax of which candles are made consist mainly of still more complex hydrocarbons similar to methane in composition.

The name paraffin has reference to the almost complete chemical indifference (*parum affinis*) of paraffin wax†; as all the terms of the series from methane upwards manifest this indifference, the name is now applied to them generally. The fact that they are thus indifferent is of significance as a proof that whatever the complexity, whatever the number of carbon and of hydrogen atoms in the hydrocarbon, the affinities of the atoms are mutually satisfied; if this were not the case, some terms would be more active chemically than others. As hydrogen atoms, *ex hypothesi*, cannot link other atoms together, it follows that in all the terms above methane the carbon atoms must be directly linked together and that only their spare affinities are satisfied by hydrogen. On these assumptions, the paraffins are formulated as chains of tetrad carbon atoms simply linked together by single affinities, thus—



But there is reason to believe that the affinities of the carbon atom can only act in certain directions and that when a number of such atoms are united together they do not form a long straight chain—an uneconomical mode of packing—but that they become

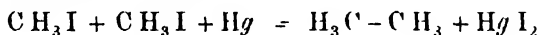
\* A variety of considerations all justify and indeed necessitate the conclusion that the hydrogen atom acts uniformly as a univalent or monad radicle.

† As *cerotic acid*,  $C_{27}H_{54}O_2$ , may be obtained by oxidising paraffin wax, it follows that hydrocarbons containing at least 27 atoms of carbon are present in the wax.

arranged spirally, so that a complex compound such as paraffin wax may be pictured as resembling a *curl* or *helix* rather than a straggling chain. The most appropriate model, in fact, that can be constructed to *symbolise the functions* of a carbon atom is a regular tetrahedron.\* And supposing the tetrahedron to be inscribed within a sphere, the four affinities of the atom may be pictured as proceeding from the centre of the sphere to the four solid angles of the tetrahedron; the angle at which two affinities meet is therefore  $109^{\circ} 28'$  and while one pair of the affinities is situated in one plane the second pair lies in a plane at right angles to the first pair.

A skeleton wire model of the carbon affinity system is easily made by bending two pieces of wire each at an angle of  $109^{\circ} 28'$  and then soldering the two pieces together at their angles so that they meet in two planes at right angles to one another; the four arms represent the affinities and the directions in which they act. Models of paraffins are easily constructed by joining the proper number of such skeleton tetrahedra together by laying an arm of one tetrahedron against an arm of another and then lashing or soldering the two together.

The representation of the carbon atoms in the paraffins as united by single affinities is but the expression of the fact that the higher hydrocarbons are prepared from the lower by displacing a single atom of hydrogen—say by a single atom of iodine—in any lower hydrocarbon, then withdrawing the iodine by means of a metal; the hydrocarbon residue thus formed at once unites with a like group formed from another molecule of the iodide. Thus, when methyl iodide from methane is exposed over mercury to sunlight, it is converted into dimethyl or ethane—



It is possible, however, not only to associate carbon atoms by single affinities in open chains or curls having their two ends free but these ends may be united together so as to form closed chains or rings (*cyclouds*). Such a ring is formed with particular readiness by the union of five carbon atoms; the hydrocarbon of these dimensions is particularly stable and unattractive, like the paraffins.

When the number of carbon atoms united in a ring is less than five, the compound is no longer unattractive but, on the contrary, is acted upon more or less readily by a variety of agents, the ring being broken in the process. Each of the angles within a regular pentagon being very nearly  $109^{\circ} 28'$  (the angle at which the affinities meet in the tetrahedron model of the carbon atom constructed in the manner described above) it is a striking fact that when five such tetrahedra are joined together they form practically a complete

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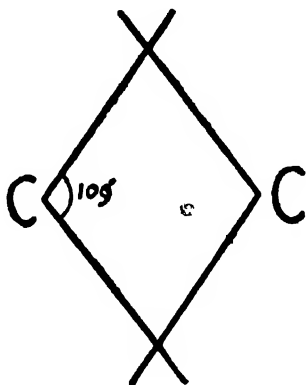
\* Such a model may be constructed of four equilateral triangles, cut out of stout cardboard, joined together at their edges so as to form a solid figure.

pentagon. Any smaller number cannot be joined together in such a way that the wires representing affinities are brought into parallelism; they can only be joined by crossing the affinities and binding them together at the junctions. The size of the angle between two affinities may be regarded as the departure from parallelism, being greater the smaller the number of atoms united, indicating in some degree the relative stability of the ring system, the approximation of the affinities being inversely proportional to the exterior angle between crossed affinities—thus

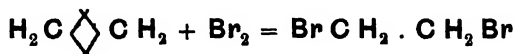
The behaviour of the closed chain hydrocarbons is in striking agreement with the geometrical peculiarities of models constructed in the manner described, so that however far removed they are from being representations of the manner in which the carbon atoms are actually combined, such models nevertheless serve a most useful purpose in indicating the peculiarities of the different types of compound.

Cycloids such as have been described are all paraffinoid compounds, in the sense that the carbon atoms are individually united in pairs by single affinities, as in the paraffins; they are also paraffinoid or saturated in the sense that they cannot enter directly into combination with other molecules; they differ from the paraffins, however, in being more or less attractive of other molecules to a greater extent than are the paraffins, which all but shun other molecules.

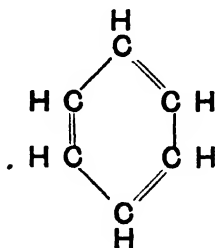
But carbon atoms may be united in pairs by more than single affinities—a fact which is clearly brought out in the tetrahedral model, as two tetrahedra may be united not only by joining an apex of the one to that of another but also by approximating an edge of the one to an edge of the other or even by bringing the triangular base of the one into contact with that of the other. Both these forms of combination are well known: the one occurs in ethene or ethylene (olefiant gas),  $C_2H_4$ , the other in acetylene,  $C_2H_2$ . When models of such compounds are made with skeleton tetrahedra, it is obvious that the affinities cannot be made to overlap and saturate one another as in the paraffins but that they can only be crossed: in other words, they saturate one another imperfectly and therefore such hydrocarbons should be attractive of other molecules, to a greater extent, moreover, than is the case with the cyclo-paraffins. In point of fact, both ethylene and acetylene behave as eminently unsaturated compounds, being, for example, immediately absorbed



by bromine and converted into derivatives of the corresponding paraffin ethane, in which the carbon atoms are united by single affinities :



The hydrocarbon discovered by Faraday in 1825, now known as *benzene* on account of its relationship to benzoic acid, has peculiar properties which distinguish it from the paraffins and the ethenes, its behaviour being apparently that of a saturated and not that of an unsaturated hydrocarbon : to judge from its composition,  $\text{C}_6\text{H}_6$ , assuming that the six carbon atoms are united together in a ring by single affinities and that six of the affinities are satisfied by hydrogen, six affinities still remain to be accounted for : as the compound appears to be saturated, these must be disposed of in some other way. There has been much dispute on this matter : Sir James Dewar, as far back as 1867\*, himself suggested a way out of the difficulty but the arguments are now against the ingenious solution of the problem which he put forward. Kekule, in 1865, enunciated his celebrated hypothesis that the carbon atoms in benzene are united in a ring alternately by single affinities as in the paraffins and by double affinities as in the ethenes ; he represented it, therefore, by the formula :—



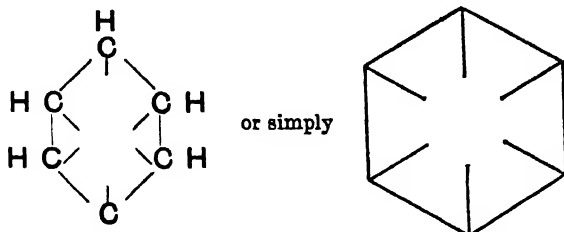
On this assumption, the behaviour of benzene should be that of ethylene exaggerated, which is in no way the case ; gradually, this objection has been recognised and Kekulé's formula no longer holds the field. At present, the tendency is to accept the centric formula as a more suitable symbol. In this the six affinities not engaged in the ring and not saturated by hydrogen are represented as acting towards a common centre and as neutralising one another by their

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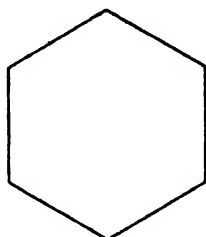
\* On the Oxidation of Phenyl Alcohol, and a Mechanical Arrangement adapted to illustrate structure in the Non-saturated Hydrocarbons. Proc. Roy. Soc. Edin. 1866-7.



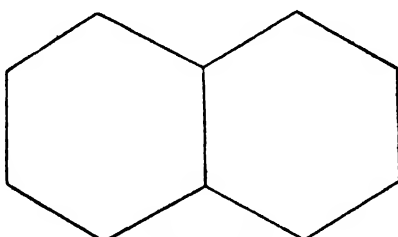
mutual influence, without, however, directly entering into combination. The symbol is written—



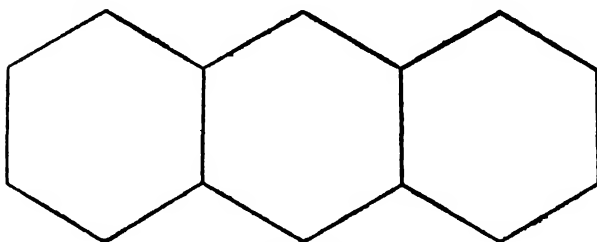
Benzene is one of the hydrocarbons which are produced in manufacturing gas by heating coal; other hydrocarbons formed at the same time are naphthalene and anthracene. It is now established that naphthalene,  $C_{10}H_8$ , may be regarded as formed by the fusion of two and anthracene,  $C_{14}H_{10}$ , of three benzene rings, thus—



Benzene



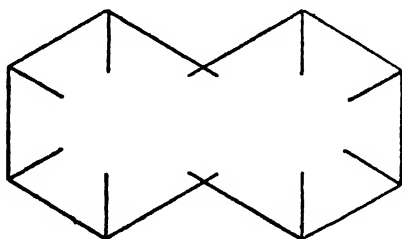
Naphthalene



Anthracene

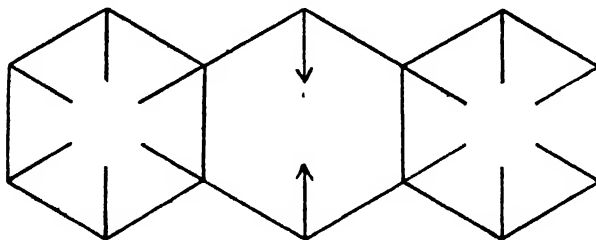
More complex hydrocarbons than these containing larger proportions of carbon and smaller proportions of hydrogen are present in coal tar, all of which apparently are built up in a similar manner: it would seem, indeed, *that the formation of carbon* from the simpler hydrocarbons involves not only the gradual loss of hydrogen but also a correlative growth in complexity, due to the fusion of ring upon ring in the manner illustrated in formulæ such as the above.

The conventional ring formulæ assigned to the benzenoid hydrocarbons, such as have been used above, however, are expressions which are to be regarded as *symbolic of the functions* of such substances rather than as absolute representations of their structure. Thus the simple hexagon by which benzene is represented above is symbolic of a symmetrical closed system. In representing naphthalene merely by two conjoined hexagons therefore, expression is given to the fact that it also functions as a symmetrical closed system. Actually, it must be supposed that it is impossible—assuming that benzene has a centric structure—to fuse two benzene rings together and yet preserve the centric structure of both. If the affinities of the carbon atom operate in any rigid manner “tetrahedrally,” the ten carbon atoms of naphthalene must form a constricted *monocycloid* system, thus—



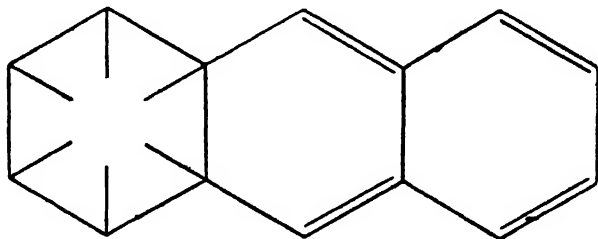
As the affinities at the waist of this system merely interlace, they do not satisfy each other; hence the unsaturated character of the molecule is represented by this formula, whilst at the same time naphthalene is shown to possess a special character of its own. Such a formula is in close accord with the general chemical behaviour of the hydrocarbon.

Anthracene,  $C_{14}H_{10}$ , may be modelled in carbon affinities in two ways, one of which is symmetrical and the other unsymmetrical:—



The first in no way corresponds to the properties of the hydrocarbon: the second, however, both gives expression to its unsym-

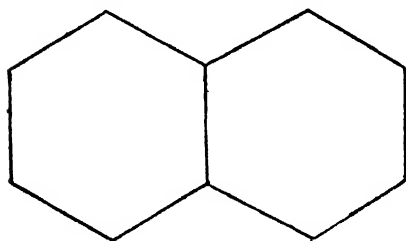
metric behaviour and is in harmony with the fact that it is a coloured substance. It will be noticed that in this formula the carbon atoms are united partly as they are in the paraffins (on the one side of the central ring), partly as in ethene, partly as in benzene. Attention



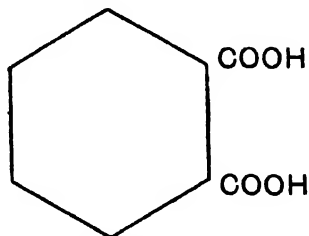
is called to these various formulæ in order that it may be clear that when a number of carbon atoms become associated they are necessarily arranged in a variety of ways.

Amorphous carbon itself is presumably but the last stage in a series of transformations, the end result being a complex in which a considerable, if not a very large, number of ring systems are so interlocked that the various affinities are all engaged. But to account for the properties of amorphous carbon, it is necessary to assume that ethenoid affinities—the unsatisfied conjoined pairs of affinities formed by the union of two carbon atoms by the partial saturation of two affinities of the one by two affinities of the other—preponderate in the molecule and come freely to the surface.

It may be pointed out that, when oxidised, naphthalene yields phthalic acid—an acid derived from benzene, thus—

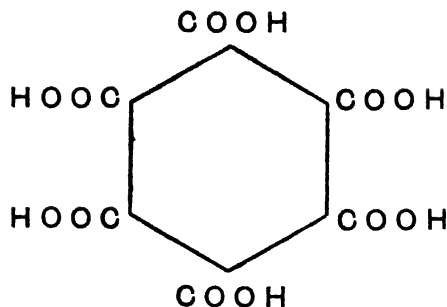


Naphthalene



Phthalic acid

Anthracene also gives rise to this acid on oxidation. Obviously, if two other systems such as that attached to one pair of carbon atoms of the centric nucleus in anthracene were attached to each of the remaining two pairs of carbon atoms in the same nucleus, a hydrocarbon would be formed capable of giving rise on oxidation to an acid of the formula—



The acid of this composition is known as *mellitic acid*; as the acid can be obtained by oxidising amorphous carbon, there is every reason to suppose that the carbon molecule in some way corresponds in structure to a hydrocarbon such as is here thought of.

*Colour of Amorphous Carbon.*—This also is a property which may be interpreted as proof that the molecule has a complex ethenoid structure.

In writing to Schönbein in 1852 Faraday remarks :—

“Your letter quite excites me and I trust you will establish undeniably your point. It would be a great thing to trace the state of combined oxygen by the colour of its compound, not only because it would show that the oxygen had a special state which could in the compound produce a special result but also because it would, as you say, make the optical effect come within the category of scientific appliances and serve the purpose of a philosophic indication and means of research, whereas it is now simply a thing to be looked at. Believing that there is nothing superfluous or deficient or accidental or indifferent in nature, I agree with you in believing that colour is essentially connected with the physical condition and nature of the body possessing it; and you will be doing a very great service to philosophy, if you give us a hint, however small it may seem at first, in the development or, as I may even say, in the perception of this connection.”

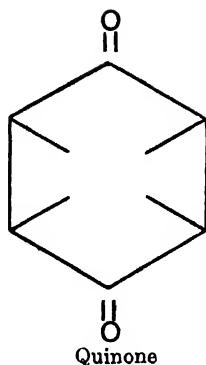
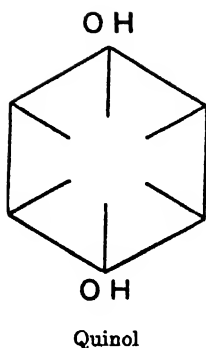
What Faraday foresaw is since come to pass. Light, it is well known, is always more or less refracted by passage through a transparent medium. Among carbon compounds the paraffins are the least refractive substances known. If certain values be taken as atomic refraction constants (comp. Brühl, these Proceedings, vol. xviii. p. 122), it is easy to deduce the molecular refractive power of any paraffin hydrocarbon and the value thus found, is in close approximation to that calculated. Carbon in the ethenoid state, however, produces a greater effect; it has the peculiarity, moreover, that when two or more pairs of ethenoid carbon atoms occur in *close conjunction* the refractive power is not merely the sum

of the refractive powers which such systems would exercise separately but always greater. The system of carbon atoms forming benzene also has a peculiar influence on light and when such systems are combined the effect they exercise is in excess of the sum of their influences apart.

Colour may even arise by the superposition of the effects produced at ethenoid junctions and in benzenoid systems—in fact, it is now beyond question that colour is conditioned by structure and it is doubtful if any really simple molecule be coloured. Although benzene and naphthalene are colourless, anthracene, as already mentioned, is coloured (pale yellowish-green); moreover it is fluorescent. It will be noticed, on reference to the formula on p. 375 that anthracene is represented as containing four ethenoid systems and a centric benzenoid system: its colour is doubtless due to the co-operation of these, each system acting as a special “light-absorbing” or resonating centre but the effect produced in this case, judging from the intensity of the colour, is not very considerable. Yellow and red hydrocarbons are also known: thus the red colouring matter of the carrot is a hydrocarbon; there is reason to suppose that the number of ethenoid and centric systems in these compounds co-operating in the production of colour is larger than in anthracene.

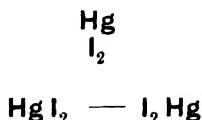
Relatively few coloured hydrocarbons are known, however. The majority of coloured organic substances are hydrocarbon derivatives containing either oxygen or nitrogen or both these elements in certain definite forms of combination. To give an example, Faraday's benzene ( $C_6H_6$ ), which although highly refractive, is colourless, is easily converted into a coloured substance by means of oxygen. By introducing in place of two of its hydrogen atoms two hydroxyl groups—that is to say, the fundamental molecule of water,  $OH_2$ , minus one of the atoms of hydrogen—*hydroquinone* or *quinol* is produced, the substance well known among photographers, who use it as a developing agent. Quinol is a non-volatile, odourless, colourless crystalline substance which dissolves easily in water. It is very sensitive to the action of oxidising agents, whereby it is at once deprived of the two atoms of hydrogen contained in the two hydroxyl groups and converted into quinone, which is so called as it was first obtained by oxidising quinic acid from cinchona bark. The change may be pictured in the manner shown on next page.

Thus represented, the change involves a striking alteration in the contexture of the molecule, in fact, the passage of the oxygen into a special state such as Faraday contemplated. Corresponding to this change, an extraordinary alteration in properties is noticeable, quinone being a deep yellow coloured, highly volatile solid, of marked odour, scarcely soluble in water. Its colour may be ascribed to the presence in the one molecule of the two ethenoid (oxygen-carbon) junctions and the benzenoid centric junction, which together



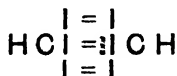
form an unsymmetrical light absorbing system. Most coloured substances appear to contain such a "quinonoid" system; even a simple substance such as iodoform,  $\text{CHI}_3$ , which has a yellow colour, may be regarded as a compound of quinonoid type, since iodine has a tendency to function as a tervalent element, so that each iodine atom in iodoform has two affinities potentially free. Normally, the single quinonoid system has a pale colour—a more or less pronounced yellow—but if additional "absorbing centres" are developed in the molecule, the colour grows in intensity and is especially intense in cases in which two or more such systems are associated.

Mercuric iodide is another case in point: in the solid state this compound is either yellow or scarlet; in the gaseous state, however, it is said to be colourless and when dissolved in certain solvents it forms colourless solutions. According to the quinonoid hypothesis, a molecule of the formula  $\text{HgI}_2$  should be colourless, like that of methylene iodide,  $\text{CH}_2\text{I}_2$ ; but if several such molecules were conjoined, thus



a system corresponding to that of quinone would be formed.

It is not improbable that the yellow colour of solid iodoform is that of a complex such as



Moreover, the blue colour of water, of oxygen and even that of ozone, in which Faraday displayed such special interest, is not improbably conditioned by the presence of molecules of a more

complex character than those represented by the conventional formulæ  $\text{OH}_2$ ,  $\text{O}_2$  and  $\text{O}_3$ .

True blacks have not yet been produced by artificial means but a number of artificial dye stuffs are known the colour of which borders on black. The almost complete absorption of light by such materials appears to be conditioned by the conjunction of a number of light-absorbing systems and the superposition of their individual absorptive effects, as they are all substances of complex benzenoid structure, containing several systems each of which taken singly would be more or less intensely coloured—usually yellow or red.

It is therefore probable that the blackness of the amorphous forms of carbon is due to its complex atomic structure and that it is composed of ethenoid-benzenoid systems similar to those which are met with in the more complex coal-tar hydrocarbons. A similar argument would lead us to attribute a complex paraffinoid structure to the diamond: it cannot well be supposed that six atoms of carbon can form a saturated system in the manner represented by Brühl (*loc. cit.*), unless, being formed under great pressure, the affinities in the diamond are forced to act in unusual directions, as in Tamman's ice of greater density than water. The fact that two atoms of nitrogen can form a saturated molecule shows the difficulty of arriving at positive conclusions in such cases, however.

Sir James Dewar's observations on the marvellous absorptive power of charcoal at low temperatures appear, in some measure, to meet with an explanation from the point of view above advocated; they at least afford strong presumptive proof that charcoal is possessed of properties such as are characteristic of ethenoid compounds.

#### CONDUCTIVITY IN HIGH CHARCOAL VACUA IN RELATION TO THE THEORY OF CHEMICAL CHANGE AND INDUCTION PHENOMENA.

Among the observations recorded by Sir James Dewar during the Septenate under discussion, there are not a few of which apparently the full significance has yet to be appreciated. Reference may first be made to a recent series of experiments in which a novel use has been made of the Crookes radiometer in determining small gas pressures. The observations show that when helium is the residuary material filling the instrument, an attached charcoal condenser cooled in liquid hydrogen is unable to absorb the gas sufficiently to diminish the pressure to such an extent that the radiometer will not rotate when the concentrated beam of an electric

arc-lamp is focused upon the black surface of the inner vanes. Even when the charcoal condenser is cooled in solid hydrogen to a temperature of about  $15^{\circ}$  absolute, the vanes of the instrument still rotate when exposed to the beam. If, however, hydrogen be the residuary gas, on cooling the charcoal condenser in liquid hydrogen the radiometer can no longer be excited into action. Tested in the ordinary way, by means of an induction coil, the bulb charged with helium, in which the radiometer vanes still rotate, appears to be "vacuous," as no discharge will pass through it.

The crucial importance of these observations lies in the fact that the method of purification adopted is so complete that all gases other than helium are removed from the sphere of action.

It is thus proved that a relatively considerable amount of gas may be present and yet no electric discharge will take place—in other words, that the passage of an electric current of high potential through a gaseous atmosphere is dependent, apparently, not on the mere presence of *one particular kind* but on that of appropriate *systems* of molecules, since it can only be supposed that the ordinary conductivity of "helium" in a tube prepared without using the very special precautions taken by Sir James Dewar is conditioned by its association with a minute proportion of some other substance—perhaps impure vapour of water.

A similar observation, which has always seemed to me to afford proof of the same kind, has been brought under notice on more than one occasion in the Royal Institution lectures—namely, the observation that when one of Sir William Crookes's tubes, containing an earth which phosphoresces on passing an electric discharge through the tube, is cooled locally by means of a wad soaked in liquid air, the discharge will no longer pass and the earth cannot be excited into phosphorescence. The ease with which the passage of the discharge is prevented is such as to leave no doubt that some quite volatile substance is present and becomes condensed on cooling the tube locally. This explanation will be the more easily accepted by those who have witnessed the striking demonstration often given by Sir James Dewar of the efficiency of liquid air as a cooling agent, which consists in placing a few cubic centimetres of the refrigerant in a depression in a flask charged with gaseous bromine at a low pressure. As the air boils away, the gaseous molecules within the flask can be visualised as rushing towards the cold surface and, as it were, falling asleep in the solid state as soon as they reach it, for all colour soon disappears from the interior of the flask, the bromine forming a dark solid patch on its side where it is cooled.

No observations which have been made of late years appear to me to be of more consequence than these two, in connection with the general problem as to the nature of the conditions determinative of the passage of an electric discharge through a gaseous atmosphere



at low pressures. In this, probably, is involved the whole question as to the existence, as actual separate entities, of the mysterious units termed electrons, to which so much is now attributed—but on the basis of experiments that, for the most part, have never involved an approach to the care taken in the inquiry now under discussion.

In discussing the problems of the atmosphere in 1902, Sir James drew attention to the auroral discharges in its upper regions and to the partial identification of the lines in the spectrum of the discharge with those given by some of the newly discovered gases, especially neon; at the same time he pointed out that we have still to account for the appearance of some of the rays of these gases and for the absence of others, particularly of all the rays of nitrogen. To quote one of his statements:—

“If we cannot give the reason of this, it is because we do not know the mechanism of luminescence—nor even when the particles which carry the electricity are themselves luminous or whether they only produce stresses causing other particles which encounter them to vibrate; yet we are certain that an electric discharge in a highly rarefied mixture of gases lights one element and not another, in a way which, to our ignorance, seems capricious.”

It may be that in the intensely cold upper regions of the atmosphere precisely those substances are absent—such as water vapour—which necessarily accompany the gases under ordinary laboratory conditions, a degree of purification being effected such as Sir James himself has demonstrated to be an effective means of stopping the discharge.

It may be added that the results under discussion are in harmony with those arrived at by Dr. H. B. Baker; in fact, the refined experiments on the influence of conducting moisture on the occurrence of chemical change in gases which Dr. Baker has carried out with such exceptional skill afford a body of evidence which, taken together with that elicited in the laboratory of the Royal Institution, should compel attention to the need of greater precaution in practice and, meanwhile, of greater caution in speculation.

Sir James Dewar has pointed out that it would be interesting to repeat light repulsion experiments in the highest attainable charcoal vacuum. Perhaps, in making this suggestion, he has in mind the possibility that the measured effects may be in part attributable to secondary causes such as are brought to light in his radiometer observations.

A similar question may be asked also with reference to the difference of electric potential which is set up when two metals are brought into contact—a subject of much controversy in the past. The one

side has held that the effect is due to "atmospheric" influences and that it is produced at the expense of some amount of chemical change; the other has regarded it as a purely inductive effect, although on this point again there is a difference of opinion as to whether or no the metals alone are concerned.

His suggestion may also be extended to a subject which occupied a large share of Faraday's thoughts—that of *inductive capacity*. The so-called specific inductive capacity of a vacuum was measured by a Committee of the British Association in 1880, soon after the introduction of the Sprengel pump had led to an improvement in the means of securing a high degree of exhaustion. The value was but slightly lower than that deduced previously from measurements in ordinary vacua (B.A. Report, 1880, p. 197). The question is whether in the highest attainable charcoal vacua the value would differ from that obtained under more ordinary conditions.

Faraday thought of induction "as in all cases an action of contiguous particles"; the power of propagation possessed by so-called insulators he called their Specific Inductive Capacity. But, as Tyndall has insisted, Faraday regarded insulators and conductors as merely the opposite terms in a series. The insulators in common use, we now know, are merely electrolytic conductors of very high resistance and the values of their Specific Inductive Capacity may be regarded as indicating their relative conductivities: if, as argued above, the passage of electricity through gases be dependent on the formation of complex conducting systems comparable with those which there is reason to believe condition the conductivity of liquid electrolytes, the probability that vacua such as Sir James Dewar has obtained would afford results different from those previously obtained is considerable: in any case it is desirable to examine into their behaviour. The whole subject is in need of further investigation, not in any dogmatic spirit but rather in that which Faraday had in mind when recommending the science of electricity as a fine and ready field of discovery—"to those philosophers who pursue the inquiry zealously yet cautiously, combining experiment with analogy, suspicious of their preconceived notions, paying more respect to a fact than a theory, not too hasty to generalise and, above all things, willing at every step to cross-examine their own opinions both by reasoning and experiment."

Although of late years electrical considerations have been introduced into chemical discussions, this has been done in so narrow a spirit that the security of our position is but little greater than when the connexion was first established by Faraday himself in his earliest researches.

The refined and laborious determinations previously made (1895-97) in the Royal Institution Laboratory of the dielectric constants of various liquids and frozen electrolytes at the low temperatures afforded

by liquid air\* have furnished results of extraordinary interest and importance. Professors Dewar and Fleming were led by their observations to the conclusion that, in all probability, at temperatures not far from the absolute zero, in the case of substances generally (other than metallic conductors), the value of the dielectric constant would be only two to three times that of a vacuum. Taking into account the very considerable difference in the results obtained on using specially purified distilled water instead of ordinary distilled water,† however, it is clear that even a minute proportion of impurity may affect the results; moreover the effect of reducing the temperature to the degree possible with liquefied hydrogen has to be ascertained. If induction through dielectrics such as water be at least mainly due to the propagation of an "electrolytic impulse," at temperatures at which all "fluidity" is destroyed and the molecules are firmly locked in their positions, no such action should be possible: the specific inductive capacity should fall at least to that of a vacuum.

It was clear to Faraday that a vacuum might have inductive capacity—that a charge might be communicated across a space devoid of conducting, contiguous particles; but he awaited proof before deciding and we cannot do otherwise than follow his example; probably we shall do well to suspend our judgment also in the case of dielectrics.

It is matter for congratulation that the laboratory in which such transcendent problems were first stated should be that in which the closest approach is being made to means of solving them.

*Chemical Interactions under Reduced Pressure.*—Sir James Dewar's observations on the interaction of sulphur and mercury and those on phosphorescence also deserve special notice from the point of view now under consideration.

If sulphur be placed at the one end and mercury at the other of a  $\cap$ -shaped tube (Fig. 9) and the tube be exhausted and sealed up, keeping the two ends in liquid air during the time required to reach a high vacuum either by means of the pump or by cooled charcoal, after several hours at the ordinary temperature the surface of the mercury appears tarnished, owing to the formation of a film of the sulphide. As the vapour pressure of mercury exceeds that of sulphur considerably, it was to be expected that the formation of sulphide would have taken place on the sulphur side; and, in fact, if the  $\cap$  tube be constricted at the bend (Fig. 10), sulphide is deposited at the bend. The molecule of sulphur is known to be complex even at temperatures considerably above its boiling-point but it is entirely resolved into simple diatomic molecules ( $S_2$ ) at high temperatures. Sir James Dewar's experiments would indicate that such simple

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\* Roy. Soc. Proc., vols. lxi. and lxii.

† Ibid., 1897, lxi. 319.

molecules are probably given off even at ordinary temperatures in a vacuum. It cannot be decided whether "moisture" was in any way concerned with the occurrence of change in these experiments; there must have been some moisture present, as cooling the tube during the exhaustion would have the effect of retaining a certain amount condensed on the cold surfaces.

An even more striking experiment described by Sir James is that with phosphorus. A bulb A of the shape shown (Fig. 11), to which is attached a chamber D containing charcoal covered with a layer of phosphoric anhydride "to absorb all traces of moisture," also a small mercury gauge G and a short capillary branch P containing a little phosphorus, having been thoroughly exhausted, is



FIG. 9.

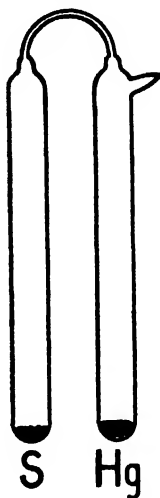


FIG. 10.

filled at atmospheric pressure with oxygen and then sealed. On immersing the charcoal chamber in liquid air the pressure soon falls to a fraction of a millimetre; then suddenly the chamber A becomes filled with a phosphorescent glow, which is clear indication of the occurrence of chemical change. The pressure having fallen to a point at which it can no longer be measured by the gauge, a stage is reached when the glow disappears and only phosphorus distills into the charcoal condenser. When the charcoal is no longer cooled and oxygen escapes from it, the phenomena are reversed: as the gas meets the phosphorus in the bulb A, the occurrence of an interaction is marked by oscillating flashes; soon all is dark again. The demonstration is a most fascinating one, as I can testify, having witnessed it several times. It may be supposed either that some particular

form of phosphorus molecule is the origin of the glow or that it marks a stage at which some special oxide is formed. The experiments of Jungfleisch lead to the conclusion that the cause of the phosphorescence is the oxidation of phosphorus anhydride, but in this apparatus no luminosity was observed when this oxide replaced the phosphorus.

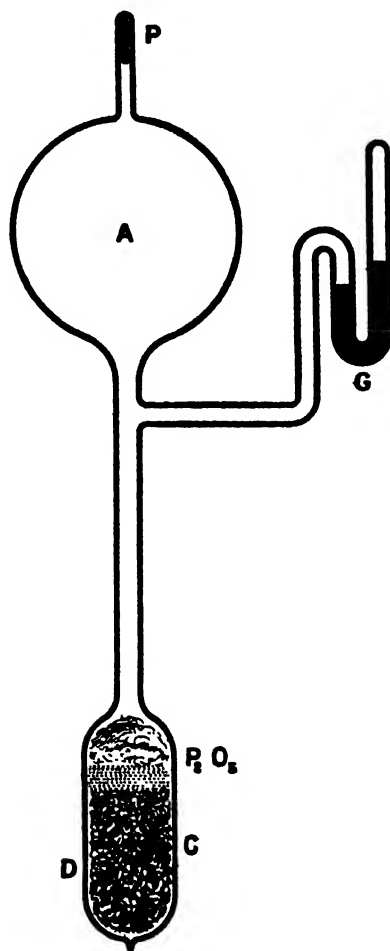


FIG. 11.

In any case, the demonstration affords a proof of the narrow range of conditions within which a particular kind of change may occur. I doubt if it afford any proof that oxidation of phosphorus can be effected in the entire absence of "moisture." Phosphoric

anhydride cannot be credited with absolute dehydrating power; and although water vapour cannot well have remained in the bulb, it must be granted that a certain proportion of simple molecules of hydrone ( $\text{OH}_2$ ) may have been present together with the phosphorus molecules. We are perhaps too much in the habit of associating the properties of water with those of the hydrone molecule: being lighter than that of most gases, the simple molecule of water must be highly volatile, although more prone than most molecules to adhere to surfaces with which it may come in contact.

*Photographic Action at Low Temperatures.*—In the Bakerian lecture delivered to the Royal Society in 1901, Sir James states that “Photographic action is still active at the temperature of boiling hydrogen although it is reduced to about half the intensity it bears at the temperature of liquid air.” This apparently is a confirmation of his previous conclusion based on experiments made with liquid air, that such action can take place at low temperatures and in absence of moisture. The subject is a difficult one to discuss, owing to our ignorance not merely of the actual nature of the effect produced by light on the sensitive silver salt but also of the nature of the active “system.” Even assuming, however, that it be the silver haloid alone, although this is *per se* an electrolyte in the viscous or fluid state, it is probably not in the rigid state; and the same argument would apply to any system composed of the haloid and a sensitiser: therefore it should not be sensitive to light at low temperatures. It is perhaps not improbable that the photographic effect is the result of autoexcitation consequent on the phosphorescence which Sir James has shown to be conditioned in so many substances by exposure to light at low temperatures.

In calling attention to the bearing of all these different results on the one problem, I am led by the desire to lay all possible emphasis on their importance and the need of further inquiry.

*Solid Fluorine.*—The liquefaction of fluorine during the earlier period has now been followed by its solidification by means of liquid hydrogen. The yellow liquid is converted into a white solid,\* melting at about  $40^\circ$  absolute, a temperature a little below that at which solid oxygen melts. When the point of a tube containing solid fluorine plunged in liquid hydrogen was broken off by means of steel pincers a violent explosion took place.

A further series of observations on the interactions of liquid fluorine with substances previously cooled in liquid air have been

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\* Chlorine also becomes white when it solidifies. In the account given to the French Academy of these experiments (*Comptes Rendus*, cxxvi. 642), it is implied that bromine is colourless when solid. This is incorrect. I am informed by Sir James Dewar that it only becomes somewhat paler in colour.

recorded. Sulphur, selenium, red phosphorus and arsenic are all violently acted upon but tellurium and antimony are not affected. Sodium is slowly attacked, potassium violently after an interval; lime is decomposed with violence and the hydrocarbon anthracene is at once acted upon. It has been argued that these observations indicate the persistence of a high degree of affinity at low temperatures but it may be questioned whether such is the case: the least change would cause the temperature to rise locally and once started might take place under "spheroidal state" conditions.

#### MODIFICATIONS IN THE PROPERTIES OF MATTER AT LOW TEMPERATURES.

*Effect of extreme Refrigeration on Alloys of Iron.*—In continuation of previous work on the strength of metals at the temperature of liquid air, Sir James Dewar and Mr. (now Sir) R. A. Hadfield have carried out a long series of observations with iron and allied metals. The results corroborate the inference previously drawn that all common metals and alloys increase in tenacity at low temperatures whereas their ductility increase or decrease, the change persisting only during the period of cooling.

In the case of Swedish charcoal-iron, the tenacity rose from 20 to 38 tons per square inch, there being substantially no elongation. Steels behaved similarly.

Nickel was improved not only in tenacity (its tensile strength being increased from 29 to 46 tons) but also in ductility (from 43 to 51 per cent.). Moreover, the ductility of all the nickel-iron alloys examined was diminished to only a moderate extent by cooling.

Era manganese steel (containing C 1.23, Mn 12.64 per cent.), which is remarkable as being non-magnetic and on account of its tenacity (56 tons) and ductility (30 per cent. elongation), when cooled to  $-185^{\circ}$ , although but slightly more tenacious was almost entirely detoughened, being elongated only to the extent of  $2\frac{1}{2}$  per cent.

The most remarkable are the iron-manganese-nickel alloys containing about 6 per cent. of manganese and from 14 to 24 per cent. of nickel. These alloys are non-magnetic and possess the highest electric resistance of any known alloys; they are also the most ductile alloys yet made. The ductility of an alloy containing about 14 per cent. of nickel was reduced by cooling from 75 to 25 per cent.; one containing about 18 per cent. decreased in ductility only from 57 to 42 per cent., whilst a third containing 24 per cent. actually rose in ductility from 60 to 67 per cent.—this being the first alloy met with which increased in ductility on cooling.

Such results are very remarkable. The magnetic properties of iron are probably not, as was at one time supposed, inherent in the

simple molecules but are characteristic of particular structural arrangements of such simple molecules; in fact the remarkable variation in properties met with among the iron alloys may well be traceable, at least in large part, to structural differences. Unfortunately such problems cannot be dealt with at present except inferentially; on this account the insight afforded by the experiments carried on at low temperatures is of very special value and interest.

*Ice at Low Temperatures.*—Water is undoubtedly one of if not the most remarkable of known substances, both in its physical and its chemical behaviour. On cooling the liquid, it ceases to contract at  $4^{\circ}\text{C.}$  and expands slightly until the freezing-point ( $0^{\circ}\text{C.}$ ) is reached, when it becomes ice; the conversion of the liquid into solid is attended by a great increase in bulk, the density of ice at  $0^{\circ}\text{C.}$  being only 0.91599 grams per cubic centimetre. There can be no doubt that ice molecules are present in solution in the liquid, it may almost be said, long before solidification sets in, the temperature at which the density of water is at a maximum ( $4^{\circ}\text{C.}$ ) being that at which the contraction which the liquid undergoes on cooling is just balanced by the expansion consequent on a certain proportion of the molecules becoming arranged in the manner in which they are present in ice.

Liquid water doubtless consists only to a limited extent of the simple molecules which constitute vaporous water, that is to say, of molecules of the composition represented by the chemical formula  $\text{OH}_2$  (hydrone); in addition to these, it probably contains complexes of several kinds formed by the association of the simple molecules of hydrone. Ice presumably is formed from some one kind of the complex molecules. In the case of oxygen as in that of carbon, there is every reason to suppose that the force of chemical affinity is exerted in certain specific directions and that when the affinities come into operation the molecules necessarily tend to assume certain relative positions. The oxygen in hydrone has a considerable amount of residual affinity, which is the cause of its activity: when owing to the reduction of temperature the vibrations of the molecules become sufficiently damped to allow the residual affinity to act, the affinities become, as it were, interlocked in certain directions and crystallisation is the consequence. Water, near to the ice point, may be likened to a pile of bricks placed one upon the other in close contact and therefore occupying minimum volume: ice may be likened to the same bricks arranged in open triangular form; so placed they enclose a hollow space and—inclusive of this space—occupy a greater volume than when placed directly one upon the other. But the formation of ice is an incomplete process of solidification; apparently ice is not a homogeneous substance but an equilibrated mixture, in certain proportions, of solid and liquid



molecules and it is to this circumstance, it may be supposed, that ice owes its peculiar viscosity and plasticity. As the temperature is lowered, the liquid molecules gradually give place to solid molecules and the ice becomes more and more nearly rigid; consequently the rate at which the volume alters diminishes as the temperature is lowered. Sir James Dewar's observations show that the density of ice at  $-185^{\circ}$  is  $0.92999$ , so that the mean cubical coefficient of change in volume between this temperature and  $0^{\circ}$  is  $0.00008099$ . This mean value is only about half that observed between  $0^{\circ}$  and  $-20^{\circ}$ , namely  $0.0001551$ . Although clear pieces of ordinary ice dropped into liquid air crack in all directions, owing to the sudden cooling, when clear pieces that have been cooled slowly in liquid air are introduced into liquid hydrogen they do not crack—this behaviour is again proof that the expansibility diminishes at very low temperatures.

As the formation of ice from liquid water involves expansion, the freezing-point is necessarily lowered by pressure; in other words, the molecules of the solid are decomposed by pressure and forced to take on some other texture. Various calculations have been made as to what would be the behaviour of water at very low temperatures and pressures, assuming that its properties change in the manner observed under more ordinary conditions; the conclusions arrived at, however, have all been upset by Tamman's remarkable observation\* that under high pressure two solid forms of water exist which are probably both denser than water; one of these melts at  $-15.8^{\circ}$  under a pressure of 5040 atmospheres. This conclusion is completely confirmed by Sir James Dewar's observation, that if water be frozen in a steel cylinder in successive portions and lead shot be included in the middle and upper portions, on cooling such ice to  $-80^{\circ}$  and subjecting it to pressure, the lead shot do not fall through the ice even under a pressure of 100 tons per square inch; it is clear that pressure does not operate to the extent formerly supposed in depressing the freezing-point of water.

It may therefore be regarded as established that chemical affinity can operate in more than one direction between the units of the water complexes and that, provided the temperature be low enough, pressure alone may be effective in curbing the tendency of affinity to act in one particular direction or set of directions and even of compelling it or enabling it to act in some other direction which is less preferred under conditions of greater freedom. The complete investigation of the optical properties of the solid forms of water at low temperatures and under various pressures would be of great interest. There is some reason to suppose that colour is more highly developed in ice than in water but I am not aware that the comparison has been made in any satisfactory manner. The molecules of hydrone *per se* should be colourless, if the explanation of the origin of colour previously

\* Ann. der Physik., 1900, ii. 1.

given be in any way correct; colour might arise, however, if several such molecules were so juxtaposed as to give rise to a system of junctions similar to those which appear to condition the appearance of colour in hydrocarbons and other compounds. The manner in which the colour of water changes as its state is varied should therefore afford some insight at least into the direction in which changes in structure are proceeding.

The alteration in colour from scarlet to yellow in the case of vermilion and of mercuric iodide and from yellow to white in the case of uranic nitrate and of ammonium platinum chloride, which is effected on cooling these substances in liquid air, may be regarded as affording proof of molecular simplification consequent on the suspension of unions of the residual affinities such as are referred to on p. 378. In the case of organic colouring matters, in which colour is conditioned by peculiarities of structure within the fundamental molecules, cooling has little if any influence on the colour.

It is when these various applications of the knowledge which is being gained of the properties of matter at low temperatures are appreciated, that the work done in the Royal Institution Laboratory is seen to be of such exceptional importance.

The determinations which have been made of the densities of oxygen, nitrogen and hydrogen in the solid state show that in these cases the density increases as the liquid becomes solid. It would be a matter of great interest if the comparison which can be made in the case of water between the solid and liquid states could be extended to other substances which are condensed only at low temperatures; at present the density of the solid in comparison with that of the liquid is known in but a few instances.

Sir James Dewar has calculated from his determinations of their densities at low temperatures that the molecular volume in the solid state—the volume occupied by the molecular proportion in grammes—of oxygen, nitrogen and hydrogen would be 21·2, 25·5 and 24·2 cubic centimetres at the absolute zero. It is interesting to note that the molecular volume of liquid hydrogen at its boiling point is 28·6, whereas that of liquid helium is 26·6. It is remarkable that the values should be so nearly alike, taking into account the great difference in the masses of the molecules.

*India-rubber at Low Temperatures.*—Perhaps the most striking case of alteration in properties effected by extreme refrigeration is afforded by india-rubber, which is one of the most elastic of substances at ordinary temperatures: when cooled in liquid air, however, it becomes so rigid and brittle that it is easily pulverised. Films 1/50 mm. thick are no longer permeable by liquid oxygen, or even liquid hydrogen. The main constituent of india-rubber is a complex hydrocarbon of the turpentine class, containing a number of ethenoid junctions; these junctions presumably determine its peculiar physical

properties and also render it a solvent of oxygen: probably these junctions become localised in their action at low temperatures, owing to some rearrangement of the molecules more or less akin to that involved in the formation of ice from liquid water. The effect produced by cold on india-rubber, it may be pointed out, is very different from that noticeable in the case of charcoal, the activity of which is also attributable to its polyethenoid structure; but in the latter case, being rigid, the ordinary molecule is probably insusceptible of rearrangement, so that the ethenoid junctions remain operative even at low temperatures. The power of condensing gases—more-over of acting as a selective “solvent”—which is exhibited by charcoal in so marked a degree, may be regarded as incipient in india-rubber, since this is a solvent of oxygen but not of other gases to any marked extent.

The manifestation of so high a degree of attraction for charcoal by hydrogen gas, as pointed out above, is proof that although it is a univalent element the biatomic molecules of the gas are possessed of residual affinity, which comes into operation when their rate of motion is sufficiently reduced by cooling.

A similar argument is applicable to helium.

#### CALORIMETRIC STUDIES.

When a volatile liquid is evaporated by passing a current of air through it, the temperature falls owing to the escape of heat in the vapour. Sir James Dewar has made a most interesting application of this principle by utilising it in solidifying liquefied nitrogen and hydrogen. If, as he has pointed out, the limit of temperature reached on evaporating a volatile liquid be contrasted with the critical temperature of the substance on the absolute scale, its value is about half the critical temperature, as shown in the following table:—

	Temperature of Evaporation	Boiling- point	Critical Temperature	Evaporation Temperature in terms of Absolute Critical Temperature
Ether . . . . .	-34°	+35°	194°	·51
Sulphur dioxide . . . . .	-50	-10	155	·52
Methyl chloride . . . . .	-55	-24	141	·53
Ammonia . . . . .	-87	-39	130	·46
Ethylene . . . . .	-132	-103	10	·50

It therefore follows that if hydrogen be bubbled through liquid nitrogen, the critical temperature of which is - 146° C. or 127° absolute, the temperature should be reduced to about  $273 - 63 = -210^{\circ}\text{C.}$  and consequently the nitrogen should freeze, as it melts

at about this temperature. Actually the solidification of liquid nitrogen is easily effected by bubbling hydrogen through it. A similar argument shows that liquefied hydrogen should be solidified by passing the more volatile helium through it, and this was found to take place when mixtures of hydrogen and helium, cooled to the temperature of exhausted liquid air, circulated through regenerator coils.

*Liquid Air and liquid Hydrogen Calorimeters.*—An achievement of great importance which comes within the period under review is the use of liquefied air and hydrogen as calorimetric substances by the evaporation of which the heat given out on cooling various substances through a known range of temperature—their heat capacities in fact—can be accurately determined.

In the case of air, the apparatus used is that shown in Fig. 12, in which B is the calorimeter—a small vacuum flask some 25–50 c.c. in

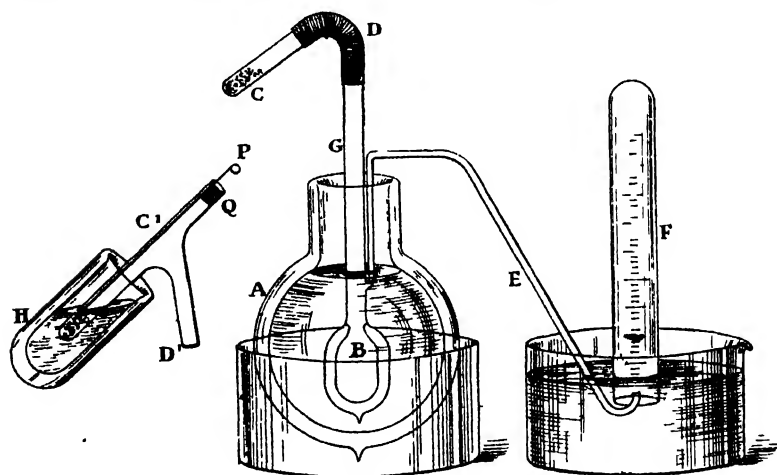


FIG. 12.

capacity—placed inside a larger vacuum vessel A, C being a tube connected with B by the flexible joint D and containing the substance to be dropped into B. The arrangement at the side represents an alternative method of introducing the substance in single pieces at a time into the calorimeter. By heating or cooling C or C', it is possible to determine the heat capacity of the substance between some particular temperature and that at which the liquid in the calorimeter boils. In practice, A is charged with a couple of litres of old liquid air rich in oxygen and some of the same liquid is introduced into B; in this way it is possible to maintain a fairly constant temperature throughout an experiment. The instrument is standardised by

dropping in a known weight of a substance of high atomic weight, such as lead, the specific heat of which varies but slightly with the temperature; the volume of gas given off is measured in the tube F.

The data in the following table illustrate the degree of sensitiveness of various liquefied gases as calorimetric agents when used in such an apparatus.

	Boiling-point	Liquid Volume in c.c. of 1 gramme at the Boiling-point	Latent Heat in gramme Calories	Volume of Gas in c.c. at 0° and 760 mm. per gramme Calorie
Sulphur dioxide . . .	+ 10·0	0·7	97·0	3·6
Carbon dioxide . . .	- 78·0	0·65 (solid)	142·4	3·6
Ethylene . . . . .	- 103·0	1·7	119·0	7·0
Oxygen . . . . .	- 182·5	0·9	53·0	13·2
Nitrogen . . . . .	- 195·6	1·3	50·0	15·9
Hydrogen . . . . .	- 252·5	14·3	125·0	88·9

It is obvious that oxygen is about twice as sensitive as ethylene, whilst hydrogen is between five and six times as sensitive as oxygen. In practice, there is an advantage in using liquefied air, as air is the substance surrounding us; when liquefied hydrogen is used, it is essential to prevent access of air to the apparatus, which may be modified for the purpose in the manner shown in Fig. 13.

Among the most interesting results obtained with these instruments are those relating to carbon—in the forms of graphite and diamond—and ice. In the case of carbon (diamond) previous determinations pointed to the disappearance of all heat capacity at about - 90°. Sir James Dewar's observations show that although the heat capacity diminishes greatly as the temperature falls, it is still perceptible in amount even at - 220°. The same is true of ice, thus:

	18° to - 78°	- 78° to - 188°	- 188° to - 252°
Diamond . . . . .	0·0794	0·0190	0·0043
Graphite . . . . .	0·1341	0·0599	0·0133
Ice . . . . .	0·463	0·285	0·146

To judge from the determinations which have been made with various substances, including those of the earlier period relating to metals, it is clear that as the absolute zero is approached the intermolecular vibrations become more and more damped and perhaps cease altogether at the zero. In the case of metals, electrical conductivity is then at its maximum but at its minimum in the case of non-metals and compound substances. To use a rough analogy in

illustration of the changes which attend the cooling, the metal molecules may be pictured as tubes provided with wide flanges,

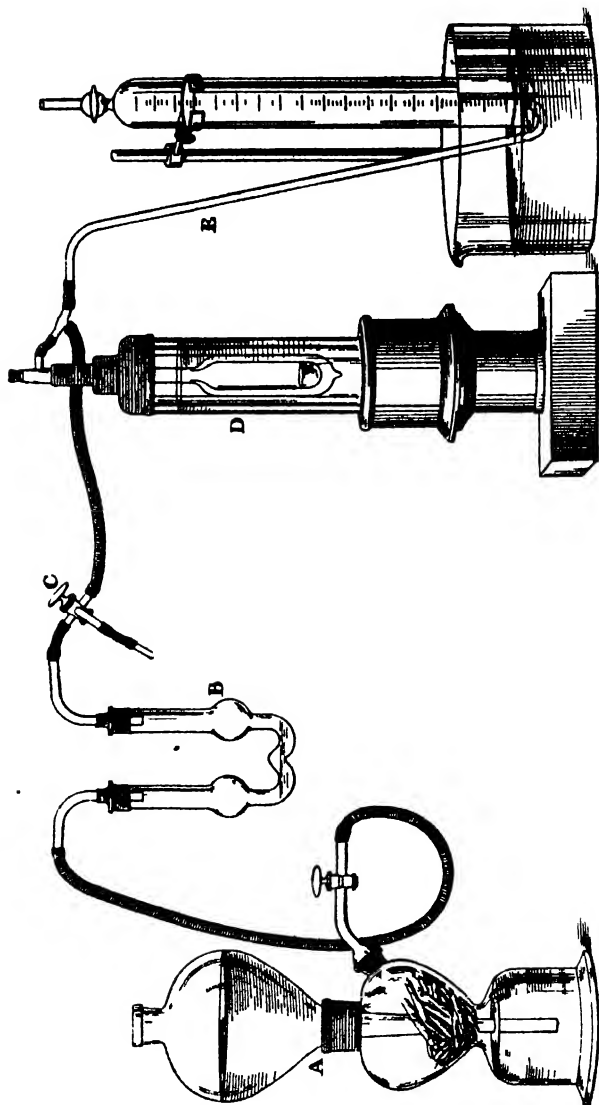


FIG 13

flange sliding on flange in such a manner that the passage of fluid through a series of connected tubes is more or less interfered with

by the oscillatory movement at each junction; as the temperature falls, the flanges come more nearly into apposition and ultimately coincide. Conductivity is then at its maximum, the rate of flow depending alone on the sectional area of the tube and the skin friction, being no longer checked by the oscillations of the tubes.

#### THERMOMETRY AT LOW TEMPERATURES.

Owing to the fact that the rate of change of resistance of platinum becomes gradually smaller at very low temperatures, the accurate determination of low degrees of temperature cannot well be effected by means of resistance thermometers.

An elaborate investigation of a number of constant pressure gas thermometers has been made from which it appears, that either a simple gas such as helium, hydrogen or oxygen or a compound gas such as carbon dioxide, at an initial pressure somewhat less than one atmosphere, may be made use of as the thermometric substance in determining temperatures near to but above that at which it boils.

The average value of the boiling point given by these experiments in the case of oxygen is  $-182^{\circ}\cdot5$  and in the case of hydrogen  $-252^{\circ}\cdot5$  or  $20^{\circ}\cdot5^*$  absolute. The value for oxygen is in agreement with the mean results obtained by Wroblewski, Olzewski and others.

The melting-point of hydrogen, determined by a helium thermometer, is  $15^{\circ}$  absolute.

A careful study of a large number of resistance thermometers has shown that at low temperatures these give variable results and that no thermometer of the kind will afford accurate values up to and below the boiling-point of hydrogen. At the boiling-point of

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\* In the interest of historical accuracy, it should be pointed out that this value was first given in the Bakerian lecture delivered to the Royal Society on February 7, 1901, published in their Proceedings, vol. lxxviii., pp. 44-54.

If reference be made to the third English edition of Ernst von Meyer's History of Chemistry from the earliest times to the present day (Macmillan), an authoritative work published in 1906, the following passage will be found (p. 523):—

"Dewar was the first to succeed in obtaining a measurable amount of liquid hydrogen (about 50 c.c. at one time) and he has since then been able to solidify it. An apparatus has also been designed by Travers by means of which liquid hydrogen can be obtained in quantity.

Liquid hydrogen is clear and colourless; it shows no absorption spectrum and the meniscus is as well defined as in the case of liquid air. The boiling-point was first determined by Dewar with a platinum resistance thermometer to be  $-238^{\circ}$  C. but more recent determinations by Travers, using a helium thermometer, have given  $-252^{\circ}\cdot5^{\circ}$  C., a number now accepted by Dewar."

As a matter of fact, Travers and Jaquerod make the following statement (p. 489) in a communication read to the Royal Society on June 19, 1902 Proceedings, vol. lxx., pp. 484):—

hydrogen, the reduction of the electric resistance of some metals is very remarkable—copper dropping to only  $1/105$ th, gold  $1/30$ th, platinum  $1/35$ th to  $1/17$ th, silver  $1/24$ th of the resistance which it has at  $0^{\circ}$ . The resistance of an unalloyed metal diminishes

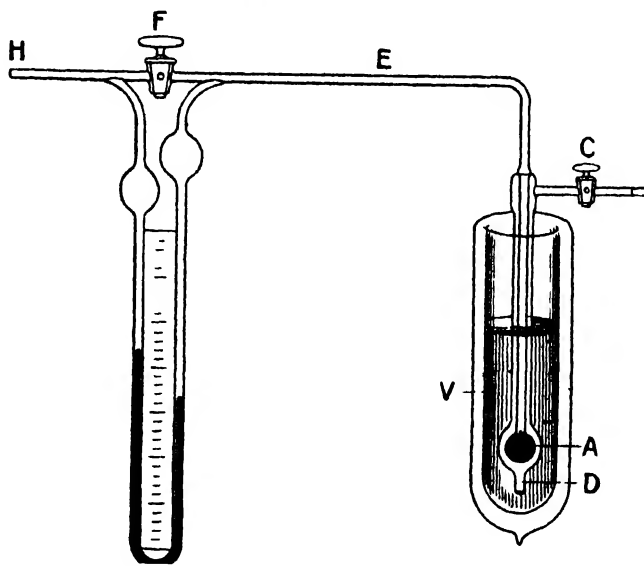


FIG. 14.

continually as the temperature falls and in each case appears to approach to a definite asymptotic limit. Gold and silver give the best measures of low temperatures. When considered in detail, the observations are full of interest as throwing light on the properties of individual metallic elements: obviously the last word on the subject has not yet been said and it is important that the inquiry should be extended to metals purified with every degree of refinement which chemical skill can devise: this, however, will be a task of great difficulty and must entail a vast amount of labour.

One of Sir James Dewar's most beautiful applications of charcoal consists in saturating it with air or hydrogen or helium and using it when thus charged as a thermometric substance. An apparatus for

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"Dewar has obtained the following values for the boiling-point of hydrogen on the constant-volume hydrogen scale —  $253^{\circ} 03$ , —  $253^{\circ} 37$ , —  $252^{\circ} 81$ , —  $250^{\circ} 35$ ; the pressure on the gas at the ice-point being 287 mm., 270 mm., 739 mm. and 127 mm., respectively. On the scale of a thermometer filled with helium containing 7 per cent. of neon, at a pressure corresponding to 728 mm. of mercury at the ice-point, he found the temperature to be  $252^{\circ} 68$  and  $252^{\circ} 84$  C."



this purpose is depicted in fig. 14. In this arrangement A is a bulb containing charcoal saturated with air or hydrogen or helium at any desired pressure; V represents liquid air or hydrogen; the space between the bulb A and D is filled with the vapour of the liquid in V. On flashing even a feeble beam of light on the bulb, although the rays must penetrate through the vessels and the liquid in V, the level of the liquid in the gauge is at once altered. The special value of such an instrument is that it becomes more sensitive as the temperature falls.

#### GASES OF THE ATMOSPHERE.

The new field opened up within recent years by Lord Rayleigh's classical discovery of argon in our atmosphere has been cultivated with such brilliant success, particularly by Sir William Ramsay and Professor Travers, that we now know that air contains besides this gas four other elementary substances: helium, neon, krypton and xenon, all of which belong to the class of inert elements—that is to say, elements which are apparently destitute of chemical properties and incapable, so far as we are at present aware, of forming compounds with other elements—unless, as may well prove to be the case, radium be a compound of helium. These gases are at present the riddles of chemistry but it may well be that their true character is not yet appreciated: indeed, presumptive proof that they are not in reality inert is afforded by the fact that they give brilliant spectra, if the argument be correct which is put forward on p. 32 that electric discharges take place in gases within complex systems. That even the helium molecule has some degree of chemical activity is shown by the fact that it is powerfully attracted by charcoal at very low temperatures and that its heat of absorption is by no means inconsiderable. Lastly, it may be pointed out that the argument which has led to the assumption being made that the molecules of these gases consist of single atoms is based on the slenderest of foundations and is entirely inconclusive—atoms possessed of an extraordinary high degree of affinity might well form molecules which would be exceptionally sluggish in chemical behaviour: nitrogen, in fact, is an illustration of the force of this argument, being almost inert in the form of diatomic molecules,  $N_2$ , although an extraordinarily active substance in the elementary state.

For these reasons the investigation of the properties of the gases of the helium group is of exceptional interest and importance.

Reference was made by Miss Clerke to the account given in 1901 by Liveing and Dewar of the separation of krypton and xenon from liquefied air by a single process of fractional distillation and of their observations on the spectra of these gases. Later observations on the separation of the various gases by means of charcoal have been referred to in an earlier section of this essay (p. 362).

In discussing the problems of the atmosphere in his Friday evening lecture in 1902, Sir James Dewar drew attention to the fact that the proportion of hydrogen constantly present in our atmosphere has been over-estimated and that there is not more than 1/900,000th of this gas in town air that has not come in contact with metal tubes.

In connection with the problem of the distribution of the minor constituents of the atmosphere, attention has been called to the conditions which affect the recognition of the various gases and to their bearing on the study of auroral discharges. The problems involving experimental study in this field are shown to be very numerous. Very striking conclusions have been arrived at as to the composition of the atmosphere in regions in which the temperature and pressure conditions are such as could not lead to the condensation of the oxygen and nitrogen.

It is probable that above fifty-six miles the atmosphere would consist substantially of the lighter gases, hydrogen and helium and neon. The effect which gradual elimination of oxygen especially would have on the colour of the sky has yet to be taken into account.

Whether other gases remain to be discovered in air is at present an open question: a considerable number of the lines seen in the spectra obtained on passing electric discharges through samples of the least condensable gases from the air are at present unidentified.

The subject of the Upper Air and Auroras is discussed very fully in Sir James Dewar's Presidential Address to the British Association at Belfast in 1902.

#### PROPERTIES OF RADIUM.

The properties of radium have been made the subject of study whenever opportunity has offered.

The heat evolved has been measured by means of the liquid oxygen and liquid hydrogen calorimeters.

It has been shown that a Blende screen, such as Sir William Crookes uses in his Spinthariscopes, is not caused to scintillate by radium if the screen be cooled in liquid air; on cooling the radium, however, both screen and radium being *in vacuo*, the scintillations are as vigorous as at ordinary temperatures. This result is at once a confirmation of previous observations that phosphorescent substances generally lose their activity when cooled to a very low temperature and a proof that radium is an entirely exceptional material.

A series of observations of striking importance has been made recently on the rate at which helium is produced from radium: these not only afford a verification of Soddy and Ramsay's discovery but also a most remarkable confirmation of the correctness of the theoretical predictions of Professor Rutherford. The experiments derive exceptional value from the fact that they were carried out with the

material purified under the direction of Dr. Thorpe, which he has shown to have an "atomic weight" practically the same as that originally deduced for radium by Madame Curie. This material was prepared at the expense of a grant of 1000*l.* made to the Royal Society by the Goldsmiths' Company specially for the purpose of promoting the study of the properties of radium—of all substances known to us the most mysterious and exceptional in its behaviour.

#### MAINTENANCE OF VITALITY AT LOW TEMPERATURES.

Dr. Macfadyen's earlier experiments on this subject were referred to by Miss Clerke. He has stated in a later communication that no impairment of the vitality of bacteria is conditioned by their continued exposure to the intense cold of liquid air even for a period of six months. That all chemical action should come to an end at such temperatures was to be expected; Dr. Macfadyen's remarkable observations, however, establish the important fact that bacteria may be frozen without being ruptured or their minute mechanism dislocated—that, in fact, they resemble in behaviour a watch, which stops when frozen, because the oil used as a lubricant is congealed, although when the temperature is raised and the oil melts it is easily started into activity from its state of suspended animation. In the organism, water is the lubricant, as it were; the once congealed organism starts into life again so soon as the water is liquid and food materials can circulate in it and gain access to the enzymic centres at which they undergo constructive and oxidative changes.

A further use has been made of liquid air by Dr. Macfadyen which may well prove to be of great importance. He has shown that by triturating micro-organisms in the hardened condition to which they are reduced by cooling in liquid air, it is possible to liberate the cell contents by purely mechanical means.

The fluid thus obtained from typhoid organisms is found to be effective as an immunising and curative agent against typhoid fever when injected into the monkey.

Moreover, it is clear that the luminosity of phosphorescent organisms referred to above is due to a vital process, as the effect is no longer noticeable after disintegrating the organisms at the temperature of liquid air.

#### THE LIQUEFACTION OF HELIUM.

The liquefaction of helium was effected on July 9th 1908, in the Physical Laboratory of the University of Leiden, by Professor Kammerlingh Onnes, who thereby achieved the conspicuous success his systematic studies of the properties of gases, carried on with great skill and unremitting perseverance during several years past, so richly deserved. In describing his results, Professor Onnes has most generously recognised the debt he is under to the Royal Institution:—

"In the execution I have availed myself of different means which Dewar has taught us to use. I have set forth the great importance of his work in the region of low temperatures in general elsewhere; here, however, I gladly avail myself of the opportunity of pointing out that his ingenious discoveries, the use of silvered vacuum glasses, the liquefaction of hydrogen, the absorption of gases in charcoal at low temperatures, together with the theory of Van der Waals, have had an important share in the liquefaction of helium."

Professor Onnes used helium extracted from Monazite sand, from which the thorium now used so largely in making the mantles for incandescent lighting is prepared. He operated with a quantity of 200 litres (160 litres being held in reserve) but it was necessary to pass this through the condensing circuit twenty times before liquefaction was observed. As showing the magnitude of his operations it may be mentioned that, at the commencement of the experiment, at 5.45 a.m., 75 litres of liquid air were available and that at 1.30 p.m. 20 litres of liquid hydrogen were ready for the final cooling operation. Nothing had been observed when the last flask of liquid hydrogen was connected with the apparatus: liquid helium was just perceived at 7.30 p.m.

In his Presidential Address to the British Association in 1902, Sir James Dewar gave a forecast of the properties of liquid helium based on his studies of the properties of the gas and the application of Van der Waal's doctrine of corresponding states, a generalisation which has played a most important part in his experiments as well as in those of Professor Onnes.

The boiling-point was estimated to be about  $5^{\circ}$  absolute; he inferred that the liquid would be twice as dense as liquid hydrogen (viz. 0.14), that it would possess a very feeble surface-tension and would be only seventeen times as dense as its vapour; also that it would be quite exceptional in its optical properties and very difficult to see.

Professor Onnes, in point of fact, had difficulty at first in realising that he had succeeded in effecting his purpose: the liquid looked, he says, at if it was almost at its critical temperature—in fact, he speaks of the peculiar appearance of the helium as being best compared with that of a meniscus of carbon dioxide in a Cagniard de la Tour tube. It has exceedingly slight capillarity. The boiling-point is at most  $4.5^{\circ}$  absolute. Liquid helium has a very low density, viz. 0.15, the ratio of the density of the vapour to that of the liquid being about 11 to 1.

The liquefaction of helium has brought us apparently to within about  $3^{\circ}$  of the absolute zero of temperature—a result nothing short of marvellous.

The history of Cold and of the Absolute Zero was discussed very fully by Sir James Dewar in his British Association Address.

He pointed out that the production of cold occupied Bacon's

thoughts and that it was made the subject of experimental inquiry by Boyle, who communicated his results to the Royal Society in 1682. Boyle's confession, that he "never handled any part of natural philosophy that was so troublesome and full of hardships," is one which probably is now thoroughly appreciated both at the Royal Institution and at Leiden.

The freezing-point and boiling-point of water were agreed upon as fixed points by the beginning of the eighteenth century. The air thermometer was first brought under notice in 1703-04 by Amontons, a French observer, whose work was not appreciated at the time. Amontons was the first to recognise that the use of air as a thermometric substance led to the inference of the existence of a zero of temperature; the value he arrived at was  $-240^{\circ}$ . More refined observations made by Lambert in 1779 gave the value  $-270^{\circ}$ , which is almost identical with  $-273^{\circ}$  now accepted.

In recent years we have learnt to do almost what we will at temperatures not far removed from this presumed absolute zero. Liquid air is now dealt with as though it were water: and from it oxygen is prepared on a commercial scale by submitting liquid air to fractional distillation, this method having superseded all others.

A long series of researches has been required to advance our command over matter at low temperatures to its present remarkable state of perfection. When the history of the subject comes to be dealt with, it will be difficult to over-estimate the importance of the contributions made from the laboratory of the Royal Institution.

#### THE FUTURE OF SCIENTIFIC RESEARCH AT THE ROYAL INSTITUTION.

Faraday, in 1813, in describing his work as chemical assistant under Sir H. Davy, spoke of himself as "constantly engaged in observing the works of Nature and tracing the manner in which she directs the arrangement and order of the world."

It may be surmised, that in giving the sum of 100,000 dollars to the Royal Institution to provide it with further means for the investigation of the relations and co-relations existing between man and his Creator, Mr. Thomas G. Hodgkins was mindful of the position in the history of scientific discovery which the Institution can claim to occupy, and was in some measure aware that it has contributed, through the work done by its professors and in its laboratories, in an altogether remarkable manner, to our knowledge of natural forces.

Nowhere else can the feeling arise in the same way in the mind of the scientific worker of being in a Holy of Holies; but how many have such a feeling? The vast import of the discoveries made within the narrow precincts of the Institution is realised probably only by very few.

Within its walls, just a century ago, Davy made the first real use of electricity as an analytical agent and discovered the alkali metals, potassium and sodium—not by any chance act, but as the result of the most careful deductive reasoning. Not content with this cardinal achievement, he subsequently demonstrated the elementary nature of chlorine and later on that of iodine, determining the properties of the latter with incredible swiftness and acumen; to crown all, he invented the safety-lamp, at the same time making no inconsiderable contribution to the theory of combustion.

Faraday—who from being a bookbinder's apprentice straightway became chemical assistant to Davy, entering at once on the path of inquiry as though to the manner born—although at first a chemist, in the course of his life, by a marvellous intuitive process, acquired mastery of the cognate subject electricity, and practically created the science. The pioneer systematic worker on the liquefaction of gases, he was also the discoverer of benzene among the products of the decomposition of oil at a red heat—the great lawgiver who defined the conditions which determine electrolytic and chemical change—the originator of new fundamental conceptions in electrical science too numerous to mention, but such that the Institution may claim to be the focus-point of the marvellous developments of pure and applied electricity witnessed during the past few decades.

That electricity owes much to the Royal Institution is generally admitted, but that the foundations of the coal-tar colour industry, with all its marvellous ramifications, as well as of a dominant section of organic chemistry—that comprising the host of descendants to which benzene has given rise—are sprung from the same Minerva head is less commonly understood; and it is yet to be recognised that the foundations of chemical belief—the conditions of chemical change—were laid down in the marvellous fifth, sixth, seventh and eighth series of Faraday's researches in electricity.

Faraday's was too simple a nature; modern conditions require more pretentious treatment than that which he inclined to adopt; his modest presentation of the facts seems no longer to catch the attention: perhaps a new generation will be more sympathetic and exploit the stores of wisdom which still lie untouched in his memoirs, when it has learnt to appreciate the spirit in which he worked—the reverent and philosophical manner in which he conducted his inquiries.

The birthplace of discoveries and inventions which have revolutionised our civilisation, it may be said of the work accomplished in the Institution that it has been the labour of the highest genius—nowhere else, indeed, can the worth of genius to the world be so clearly demonstrated. Davy and Faraday shine forth in its history and in the history of science as stars of the first magnitude—yet both came to their work untrained, with minds uninfluenced by dogmatic teaching. At the present day it is worth our while to remember this,

and to ask ourselves whether genius be not too often maimed and not made by "education." Taking into account the large number of workers now engaged in scientific inquiry, the comparatively low average of quality attained to in the output is somewhat surprising; the majority appear to lack not only originality and breadth, but also the critical faculty and that sense of proportion which is so eminently characteristic of Faraday's writings. Some occult influence is at work tending to depress the value of human effort; the distance between those who are really pioneer workers and the general body appears to be widening, not diminishing, as it should be if effective means were being taken to inform and instruct the public.

It would almost seem that, as Wordsworth has it—

. . . for everything we are out of tune;  
It moves us not . . .

in the sense, that we are not yet attuned to the complexities of modern knowledge; that in our attempt to grasp facts we lose sight of relations and co-relations; and that men like Mr. Hodgkins, looking on from a distance, have seen this and desired to assist in bringing about a better understanding.

His history appears to have been a remarkable one. Born in this country, he emigrated while young to America and established a confectionery business in New York; having made a fortune, he retired when about sixty years old and took to farming on the coast of Long Island. He died in December 1892, shortly after he had transferred to the Royal Institution the sum of 100,000 dollars United States currency, the income whereof was to be devoted (at his demise) to the purposes of scientific investigation. He was also the donor of 40,000*l.* to the Smithsonian Institution at Washington.

It would be interesting if we knew how he was moved to take so great an interest in science. Liebig, who visited Faraday in 1844, wrote to him on his return to Germany:—

"What struck me most in England was the perception that only those works which have a practical tendency awake attention and command respect; while the purely scientific, which possess far greater merit, are almost unknown. And yet the latter are the proper and true source from which the others flow. Practice alone can never lead to the discovery of a truth or a principle. In Germany it is quite the contrary. Here, in the eyes of scientific men, no value or at least but a trifling one is placed on the practical results. The enrichment of science is alone considered worthy of attention. I do not mean to say that this is better; for both nations the *golden medium* would certainly be a real good fortune."

Very largely owing to his influence and more particularly in consequence of the introduction into the University system of experimental research work such as Liebig first made possible by

training competent teachers in his laboratory at Giessen, Germany long ago changed her attitude and soon attained to the "golden medium;" the result has been that she now holds a leading position both as a cultured and as an industrial nation. But although inspired primarily by Liebig, German success cannot be regarded otherwise than as resting largely upon Faraday's work—especially upon his discovery of benzene, the study of which has profited both science and industry in a manner without parallel in any other branch of natural knowledge.

Here it is still true that only those works which have a practical tendency or sensational discoveries awaken attention and command respect; the purely scientific achievements are almost unknown. In fact, the Royal Institution is still the only establishment within whose audience chamber due public recognition is accorded to scientific work.

In giving evidence before the Public School Commission in 1862, Faraday made the weighty statement:—

"that the natural knowledge which has been given to the world during the last fifty years, I may say, should remain untouched and that no sufficient attempt should be made to convey it to the young mind growing up and obtaining its first views of these things is to me a matter so strange that I find it difficult to understand; though I think I see the opposition breaking away, it is yet a very hard one to be overcome. That it ought to be overcome I have not the least doubt in the world."

Now, nearly fifty years later, we are more than ever constrained to admit that the opposition is a very hard one to be overcome; it is breaking away perhaps a little less slowly than in Faraday's time, but much too slowly in view of past delay and our urgent needs. And the outlook at present is far from encouraging.

"Science," it is true, has been introduced into a large number of schools, but in too many cases, it is to be feared, the teaching is of a more or less perfunctory character and both poor as discipline and barren of interest. The Universities have not yet thought it well to treat training in scientific method as a necessary element of preliminary education. And at the Universities themselves mere knowledge has been cultivated at the expense of appreciation and the power of applying knowledge. Even scientific workers seem rarely to have been actuated by the spirit of self-abnegation in the public interest, having done little to overcome the resistance which the conservative elements of society oppose to progress. The effect of scientific training and work in broadening sympathies has been strangely disappointing in this respect. But Faraday appears to have foreseen that such would be the case. One of the most striking addresses he delivered of which we have cognizance was that on the "Inertia of the Mind," written in his youthful days: in this he



draws a parallel between the inertia of the mind and the inertia of matter;\* the dual state of mind which he pictures is still with us and doubtless will ever remain; it is at bottom both the cause of our difficulty and our hope. In fact, in saying that—

“the man who has once turned his mind to an art goes on more and more improving in it; the man who once begins to observe rapidly improves in the faculty . . . every little delay illustrates more or less the inertia of the passive mind; every new observation, every great discovery, that of the active mind,”

Faraday has himself pointed the way of improvement.

In 1854, when lecturing on Mental Education before His Royal Highness the Prince Consort, he drew attention to what appeared to him to be the great deficiency in the exercise of the mental powers in every direction. These words he said would express it, “*deficiency of judgment.*”

“I know,” he added, “that multitudes are ready to draw conclusions who have little or no power of judgment in the cases; that the same is true of other departments of knowledge; and that generally mankind is willing to leave the faculties which relate to judgment almost entirely uneducated and their decisions at the mercy of ignorance, prepossessions, the passions or even accident.”

He laid down what a man may and ought to do for himself in the following words:—

“It is necessary that a man *examine himself* and that not carelessly. On the contrary, as he advances, he should become more and more strict, till he ultimately prove a sharper critic to himself than anyone else can be; and he ought to intend this, for so far as he consciously falls short of it he acknowledges that others may have reason on their side when they criticise him. A first result of this habit of mind will be an internal conviction of *ignorance in many things respecting which his neighbours are taught* and that his opinions and conclusions on such matters ought to be advanced with reservation. A mind so disciplined will be open to correction upon good grounds in all things—even to those it is best acquainted with and should familiarise itself with the idea of such being the case: for though it sees no reason to suppose itself in error, yet the possibility exists. The mind is not enfeebled by this internal admission but strengthened: for if it cannot distinguish proportionately between the probable right and wrong of things known imperfectly, it will tend either to be rash or hesitate; whilst that which admits the due amount of probability is likely to be justified in the end. It is right that we should stand by and act on our principles but not right to hold them in obstinate blindness or retain them when proved to be erroneous.”

It is a sad reflection that so little attention has been paid to the lament to which he gave utterance at the conclusion of his address:—

"It is an extraordinary thing, that man with a mind so wonderful that there is nothing to compare with it elsewhere in the known creation should leave it to run wild in respect of its highest elements and qualities. He has powers of comparison and judgment by which his final resolves and all those acts of his material system which distinguish him from the brutes are guided :—shall he omit to educate and improve them when education can do much? Is it towards the very principles and privileges that distinguish him above other creatures, he should feel indifference? Because the education is internal, it is not the less needful; nor is it more the duty of a man that he should cause his child to be taught than that he should teach himself. Indolence may tempt him to neglect the self-examination and experience which form his school and weariness may induce the evasion of the necessary practices but surely a thought of the prize should suffice to stimulate him to the requisite exertion; and to those who reflect upon the many hours and days devoted by a lover of sweet sounds to gain a moderate facility upon a mere mechanical instrument, it ought to bring a correcting blush of shame, if they feel convicted of neglecting the beautiful living instrument wherein play all the powers of the mind"

The two essays to which I have referred - that written in 1823, almost at the beginning of his career and the second written thirty years later towards the close of his wonderful activity, during which period Faraday had worked with a logical clearness of purpose and a degree of constancy and consistency almost unparalleled in history—embody a complete doctrine of education; but they remain practically unheeded.

Yet such matters are of consequence, especially to the Royal Institution. Nowhere else has Faraday's doctrine been exemplified more often or more successfully. Surely some effort should be made to bring home to a larger public the mine of wealth which has been opened out by its officers, and to render it of permanent avail in the service of our nation. It needs members and it needs means: the great work done by the Institution in the past and that which, if only properly supported, it is obviously destined by its past to accomplish in the future should be more clearly and generally recognised; something more should be done to overcome public apathy to the progress of science.

It cannot but be supposed that if the interest attaching to scientific discovery were appreciated by the educated classes at large there would be a strong general desire both to be improved and to promote and subsidise inquiry. And workers should be attracted. It was, I believe, in the expectation that the attention which, he supposed, was being given in the public schools to science would lead not a few, who had both leisure and means, to desire to continue their studies and eventually devote themselves to research work, that Dr. Mond was led to establish the Davy-Faraday laboratory. Unfortunately, his expectation has in no way been justified.

In point of fact, the scientific amateur, who has been the glory of our country in the past, seems to be in danger of submergence. Some other influence than mere inertia is clearly at work, affecting intelligence and actively degrading if not destroying it. There can be little doubt that this is to be sought in two directions: in our continued belief in classical study as an effective means of education and in our insensate worship of examinations. The combined effect of these two influences is undoubtedly to develop the passive habit of mind and the belief in precedent—to cultivate the worst form of mental inertia.

The case was stated very clearly to the members of the Institution on January 31, 1868, in a Friday evening discourse, by the Rev. F. W. Farrar, M.A., F.R.S., then a classical master in Harrow School, afterwards Dean Farrar. His words are so pregnant with meaning that I feel impelled to quote them:—

“So far from being half finished, the real battle for educational reform has hardly begun. Latin and Greek still continue to be the all but exclusive staple of our education and though a classical training conducted on wise principles and with reasonable methods is of the highest value, yet the many and serious evils which our present system of it involves have been resolutely ignored. The yoke of the Greek and Latin languages have been made needlessly humiliating and needlessly heavy; taken alone, it is doubtful whether they furnish the best mental discipline for any but certain that they do not furnish even a good discipline for all; and they remain to this day entrenched behind a mountain-heap of fallacies of which no small number ought to have been banished ignominiously to the region of the most exploded errors.

“But even if all the arguments in favour of a purely classical education were as tenable as half of them are fantastic, our present system of it is a complete and disastrous failure; and that it is so may be largely demonstrated alike by the criticism of its enemies and the repeated confessions of its friends. And if this be so, it is our clear duty as Englishmen, as patriots, nay even as mere honest men, to make that system more worthy of its immense importance and of our national prestige.

“It would be easy to adduce the testimony of many eminent scholars to the humiliating ignorance on a multitude of subjects which has been the inevitable result of years exclusively devoted to two dead languages; but the case of the vast majority of boys who do not become scholars in any sense of the word is still more to be deplored. People read glowing estimates of Greek and Roman literature and take them for a delusion of classical education. There could not be a greater delusion. Hundreds of boys after years of expensive training know far less and have far less culture than their sisters who have only had the modest aid of a single governess. They know nothing except, perhaps, the merest and most useless smattering of modern languages, of history, of mathematics or of science; and if they want to pass in a competitive examination they must be hastily sent to some professional tutor to have their minds crammed for the purpose like a hurriedly-packed portmanteau. The parent comforts himself that their education has been purely literary,

but this purely literary education has somehow left them with a bad handwriting, with very vague notions of spelling and with minds that can find satisfaction in nothing higher than sensational novels. The parent takes refuge in the belief that at least their boys know Latin and Greek; but this is infinitely far from being the case; of the vocabulary they possibly know a little but of the grammar less and of the literature nothing at all. It is certain that they will never open a Greek or Latin book again; and for these paltry and miserable results they have all but sacrificed the happy seed time during which so much might have been accomplished. The evidence of these facts, evidence given by most friendly witnesses, stands in the Commission Reports undisputed and undisputable. It shows that for many a boy the years of school life are wasted. It is as though he stood in the middle of a boundless plain, waving on every side with golden corn, in the midst of which, trained to despise the sickle as vulgar and the harvest as utilitarian, he had been taught for years to occupy his time in plucking a few petals of the scarlet poppies, which are crumpled as he gathers them and which grow rank and flaccid even during the few moments he holds them in his hand.

"The question then is, not whether the education is to be literary or scientific but whether it is to be scientific or nil; the struggle is not between science and literature but between something and nothing, between science and no science, between intellectual culture and its almost total absence. It is a melancholy fact but it is a fact, that at present we struggle almost in vain against the two potent elements of intellectual progress—extravagant athleticism on the one hand and promiscuous sensation reading on the other, of which the one poisons and effeminates the mind, the other often tasks and overstrains the body; the one absorbs the strenuous ambition which might have been devoted to nobler objects, the other wastes the inestimable leisure which might else have been rich in mental and moral benefits for our country and for mankind.

"What, then, is to be done? Some would say, 'Substitute for your simulacrum of Greek and Latin an education which, if less pretentious, shall at least be real and sound, in modern languages, in literature and, above all, in science.' But it would be a great disaster if there were supposed to be any antagonism between science and literature—both are indispensable, each of them is an absolutely essential factor in an education pretending to be liberal. Yet our present system is neither literary nor scientific, whereas it is perfectly certain that it might be both."

Those who are conversant with our educational system are only too well aware that the indictment laid by the late Dean forty years ago accurately represents the position at the present day. Our "system" is still neither literary nor scientific—the fact is, we have no system: yet we have experience enough to frame one, if we could only agree to work together and to utilise our knowledge—if we could only establish the necessary organisation. Our present tendency, however, is to cast experience to the winds.

"The Greeks were themselves illiterate," said the Rev. Mr. Farrar; "they knew little of *words*, but they made up for it by *thought*—by that power of deep reflection which makes facts luminous with

meaning." We teach *words* in our schools but not *thought*. School education is a bane rather than a blessing. In consequence of lack of training in method, even scientific workers, for the most part, are content to be advocates, and too many make no attempt to exercise judicial functions or to follow in the wake of Faraday and Darwin by striving to be philosophical.

The origin of our difficulty, perhaps, is not far to seek—indeed, it is practically certain that it lies in the circumstance that our country is dominated by the literary and not by the practical type of mind, by men of narrow purview. This is especially true of our ancient Universities, by whom all affairs educational are controlled.

There can be little doubt that until the literati are deposed from their position of almost exclusive control general progress will be impossible: they will never see eye to eye with those trained on the scientific side, not from any unwillingness or ill-feeling but from actual inability to understand and appreciate their work and aspirations; the methods of the scientific worker make no appeal to the literary student: he has no conception of an experiment, and even results rarely have any significance in his eyes. Unless, therefore, it can be recognised by a preponderant party that a change must be made in the attitude of our schools and that change be enforced, nothing effective will be done. We need to put men in control who are gifted with broader sympathies than those can be who have been selected on the narrow basis of a limited literary proficiency.

In an article by Carl Snyder entitled "America's Inferior Place in the Scientific World," published in the January, 1902, number of the *North American Review*, the statement is made that, "It would be hardly too much to say that during the hundred years of its existence the Royal Institution alone has done more for English science than all of the English Universities put together. This is certainly true with regard to British industry, for it was here that the discoveries of Faraday were made."

Sir James Dewar was led by this to inquire into the total expenditure of the Institution on experimental inquiry and public demonstrations during the whole of the nineteenth century, and in his Presidential Address at the British Association at Belfast in 1902, he published the following statement of the items:—

	£
Professors' Salaries—Physics and Chemistry ..	54,600
Laboratory Expenditure .. .. .	24,430
Assistants' Salaries .. .. .	21,590
Total for one hundred years ..	<u>£100,620</u>

In addition, he said, the members and friends of the Institution have contributed to a fund for exceptional expenditure for Experimental Research the sum of £9580. It should also be mentioned that a

Civil List pension of £300 was granted to Faraday in 1853 and was continued during twenty-seven years of active work and five years of retirement. Thirty-two years in all, at £300 a year, make a sum of £9600, representing the national donation; added to the amount of expenditure just stated, this brings up the total cost of a century of scientific work in the laboratories of the Royal Institution, together with public demonstrations, to £119,800; an average of £1200 per annum.

Such expenditure has only been made possible by frequent donations from members and friends of the Institution.

Up to the present time, the work has been done by men who have been prominent as philosophers; the problem of the future will be to maintain continuity with the past, which must prove very difficult in face of an ever-growing outside competition and the increasing cost of experimental inquiry.

Future workers should not only have the necessary working space and adequate means of meeting the expenses of the position and of all inquiries which it may appear desirable to undertake; they will also need the assistance and society of competent associate workers. It should not be forgotten that the Institution will probably afford the one haven of rest open to an inquirer in our country, where original work can be done under proper conditions, undisturbed by outside influences. In all our Colleges the burden of teaching now cast upon the Professoriate is such as to render the task of research very difficult, the necessary leisure for quiet reflection and study being secured, if at all, with utmost difficulty; and student assistants are no sooner trained to the point of efficiency than they are tempted away to some remunerative post, usually before they have developed sufficient judgment and independence to become original inquirers themselves.

It is to be hoped that in the near future a sufficient staff of student assistants may be at the disposal of the Professor in charge of the Institution laboratories to aid him in the promotion of inquiry, by association with whom he will be able also to secure scientific companionship and the inspiration which naturally springs from intercourse with active youthful minds anxious to exploit the genius of their teacher. It is more than unfortunate that such assistance has not been at the disposal of the Professor of late years, both to enable him to utilise more fully the invaluable experience which he has accumulated and to have preserved this for the use of future workers.

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